

Reaction Kinetics of Jet Fuels

Hai Wang

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The JetSurF Experience

The screenshot shows a Safari browser window with the address bar displaying <http://melchior.usc.edu/JetSurF/>. The page features logos for USC, Stanford University, Princeton University, NIST, Drexel University, Imperial College London, and the University of Michigan. The main heading is "JetSurF – A Jet Surrogate Fuel Model". The text describes the model as a detailed chemical reaction model for jet-fuel surrogate combustion, developed through a multi-university research collaboration funded by the Air Force Office of Scientific Research. A list of project participants includes F. N. Egolfopoulos, Hai Wang, R. K. Hanson, D. F. Davidson, C. T. Bowman, H. Pitsch, C. K. Law, N. P. Cernansky, D. L. Miller, W. Tsang, R. P. Lindstedt, and A. Violi, each with their respective university affiliation. The page also lists releases: "New Release: JetSurF Version 2.0 – A working model for the combustion of n-alkane up to n-dodecane, cyclohexane, and mono-alkylated cyclohexane up to n-butyl-cyclohexane (Release Date: September 19, 2010)" and "Old Releases: JetSurF Version 1.1 – A interim model for the combustion of n-butyl-, n-propyl-, ethyl-, and methyl-cyclohexane and cyclohexane (Release Date: September 15, 2009); JetSurF Version 1.0 – A working model for n-alkane combustion (Release Date: September 15, 2009); JetSurF Version 0.2 (Release Date: September 8, 2009)".

JetSurF – A Jet Surrogate Fuel Model

JetSurF is a detailed chemical reaction model for the combustion of jet-fuel surrogate. The model is being developed through a multi-university research collaboration and is funded by the [Air Force Office of Scientific Research](#). Project participants include

F. N. Egolfopoulos , Hai Wang	University of Southern California
R. K. Hanson , D. F. Davidson , C. T. Bowman , H. Pitsch	Stanford University
C. K. Law	Princeton University
N. P. Cernansky , D. L. Miller	Drexel University
W. Tsang	National Institute of Standards and Technology
R. P. Lindstedt	Imperial College, London
A. Violi	University of Michigan

New Release: [JetSurF Version 2.0 – A working model for the combustion of n-alkane up to n-dodecane, cyclohexane, and mono-alkylated cyclohexane up to n-butyl-cyclohexane](#)
(Release Date: September 19, 2010)

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The JetSurF Experience

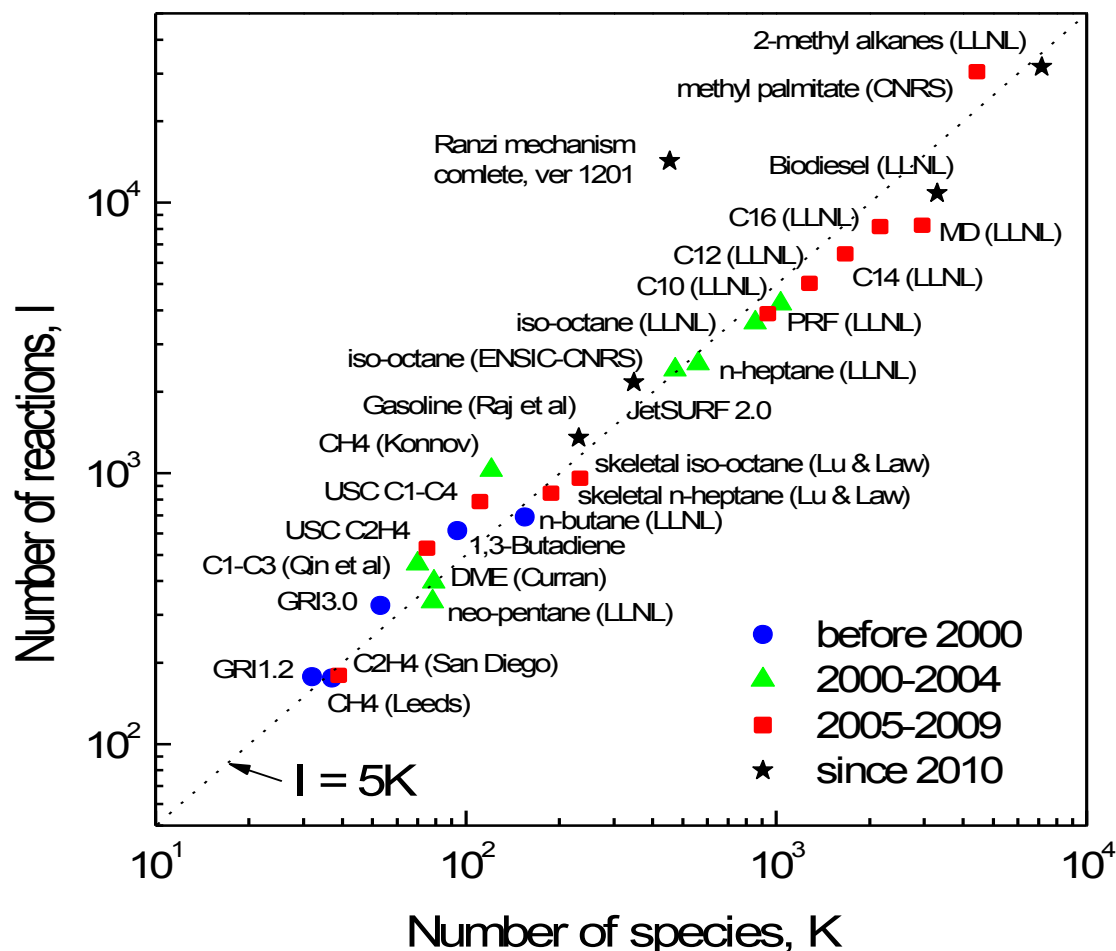
- **JetSurF 2.0**: 2163 reactions and 348 species;
- ***n*-alkane series**: *n*-pentane to ***n*-dodecane**.
- **Cyclohexane series**: cyclohexane and its monoalkylated derivatives up to ***n*-butylcyclohexane**.
- **Benzene** and **toluene** chemistry.
- **H₂/CO/C₁-C₄** chemistry.
- Validation tests for > 170 separate sets of data (documented on the web – additional tests from IPT Pls' publications).
- Web releases only.
- The JetSurF experience: our approach will not lead to a closure to a quantitative description of jet fuel chemistry.

Challenges in Reaction Mechanism Development

- **Methodology extends from Dixon-Lewis' s work some 50 years ago.**
 - Write down every reaction step and find its rate coefficient.
 - H_2 , H_2/CO etc with ~ 2 dozen reactions.
 - Can have a closure because of a limited number of rate parameters.
 - Allowed us to understand the detailed laminar flame structure.
- **Later work focused on small hydrocarbons – $\text{O}(100)$ reactions – many of which have been probed by experiments and rate theory calculations.**
- **Recent effort for large hydrocarbons – $\text{O}(10^3\text{-}10^4)$ reactions – largely based on empirical knowledge.**
 - Group additivity
 - Analogous reactions – reaction class
 - Guesses
 - Sensitivity analysis – you get information from what you put in.
 - Uncertainty analysis – try to assess and constrain uncertainty in our kinetic knowledge

Challenges in Reaction Mechanism Development

- The number of species/reactions increases exponentially as the fuel size increases, reaching $O(10^4)$ for practical fuels.



- The approach of detailed kinetic modeling is based on the notion that each and every rate parameters can be probed experimentally and/or theoretically. Hence, all model parameters and assumptions can be verified.
- The problem is a practical one – how do we verify the accuracy of the large number of assumptions/pathways/parameters?

An updated version of Lu & Law (2009)

The JetSurF Experience

Objective 1 – Qualitative Insights

- What chemistry causes faster ignition delay?
- Why a certain fuel propagates a flame faster than another?
- What does blending do to various combustion behaviors?
- What chemistry leads to increased low-T reactivity and why?
-

Objective 2 – Quantitative Predictions

- > 95% reaction pathways/rates have are assumed.
- Lumping/reaction class assumption falls apart for unimolecular and chemically activated reactions.
- Uncertainties in $k(T,p)$ are too large to pin the predictions.
- Fundamentally an ill-defined mathematic problem – ab initio theories and uncertainty quantification can't address all of the issues at this time.
- Kinetic coupling – a large thermodynamic condition space: can we test it all?

The JetSurF Experience

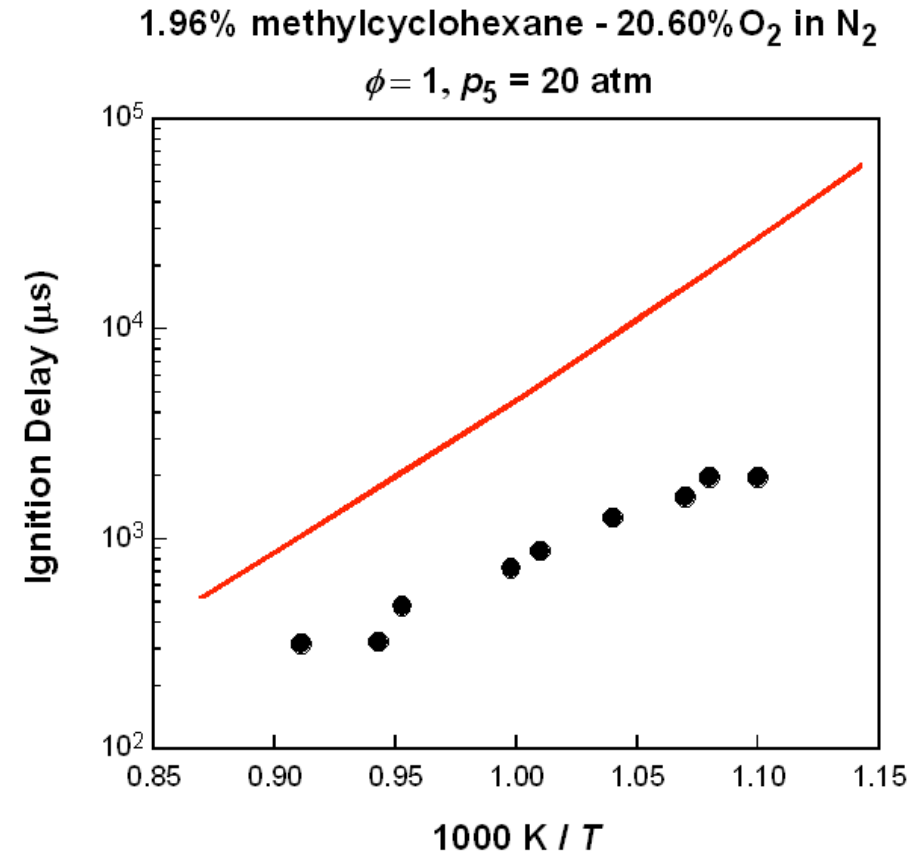
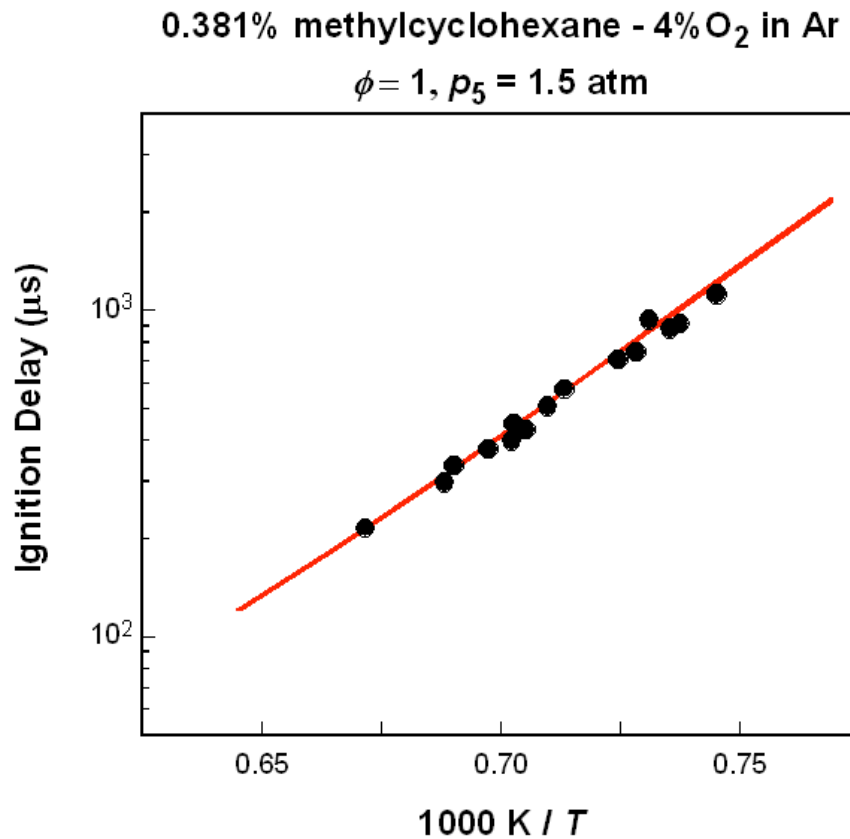
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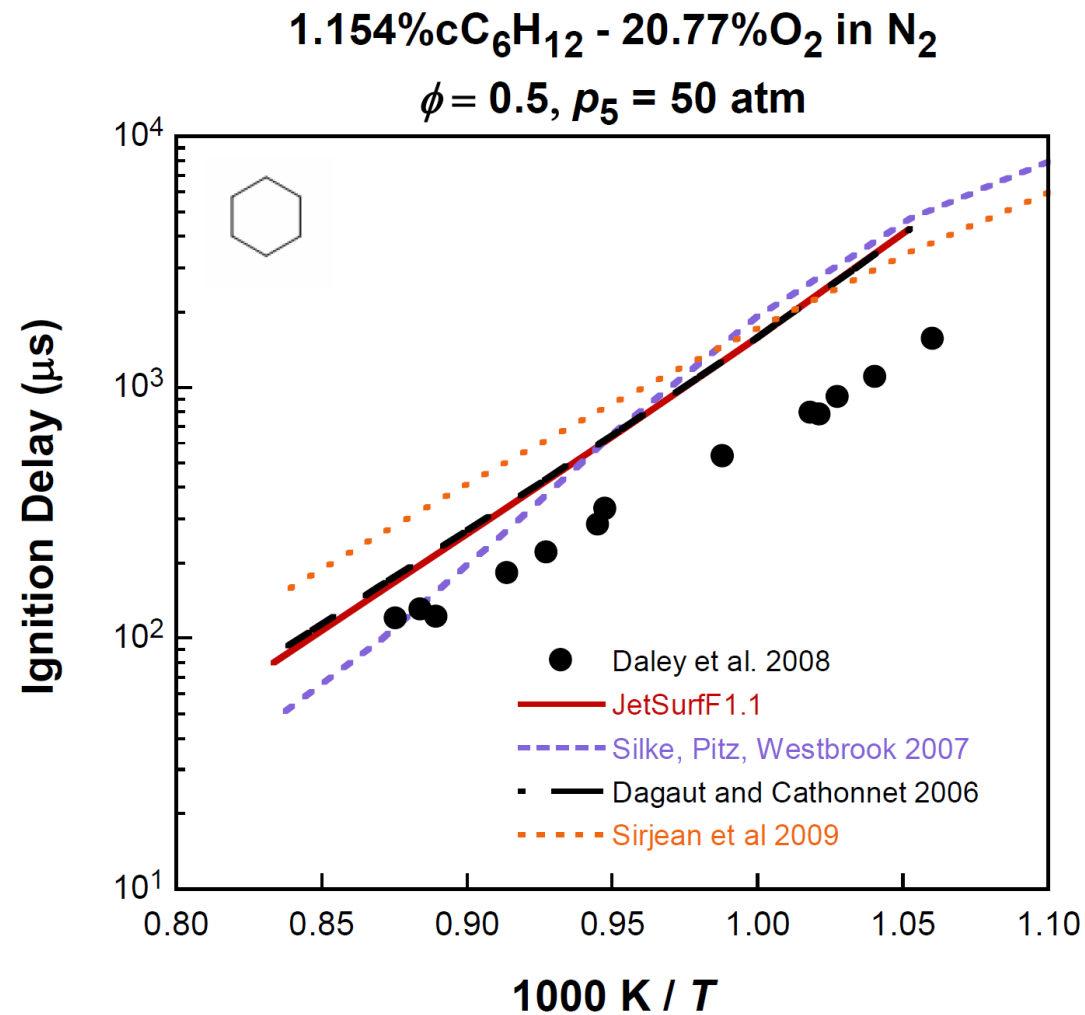
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The JetSurF Experience



Symbols: experimental data (Hanson 2009); Lines: JetSurF1.1

The JetSurF Experience

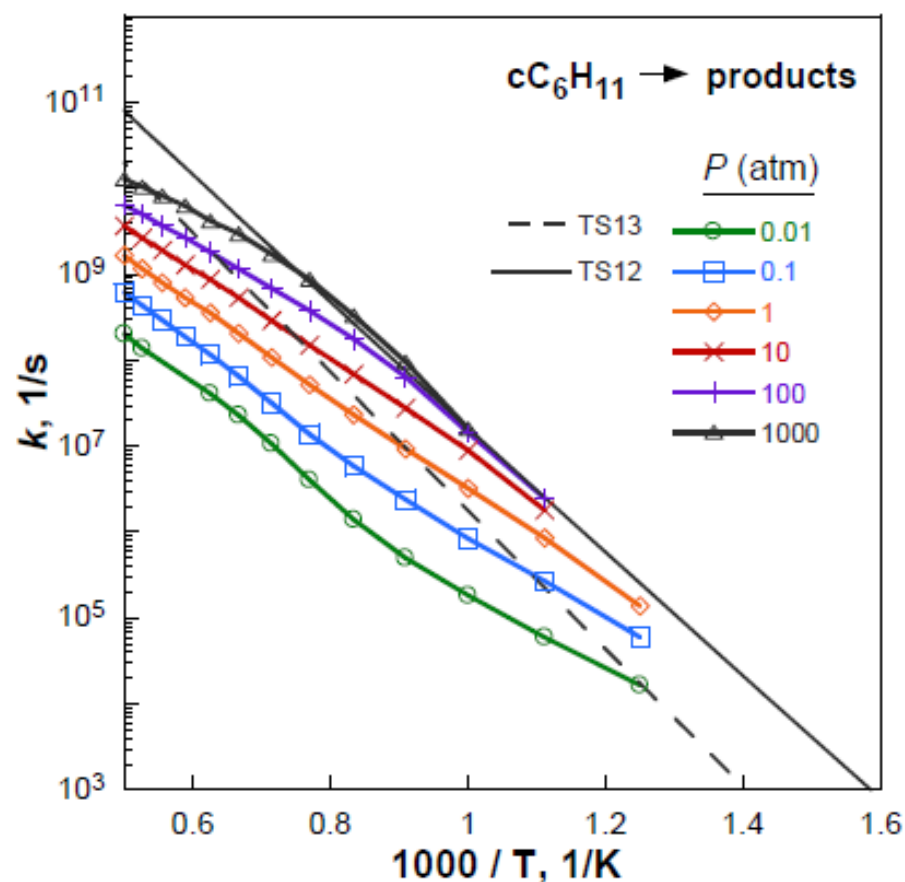
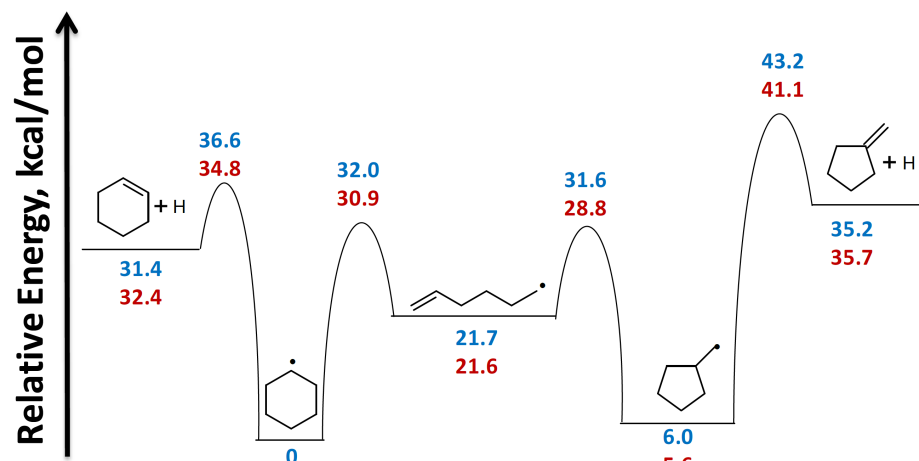


Other models have the same problem!

The JetSurF Experience

- Rate coefficients often show non-Arrhenius behaviors – lumping/class assignments are inaccurate.

Thermal decomposition of the cyclohexyl radical



The JetSurF Experience

- For many fuels, a detailed treatment of the reaction kinetics is challenging, if not impossible.

MCHX dehydrogenation reactions

-H (by H,OH,O,CH₃)

H-elimination
(P-dependent)

Reactions not shown:

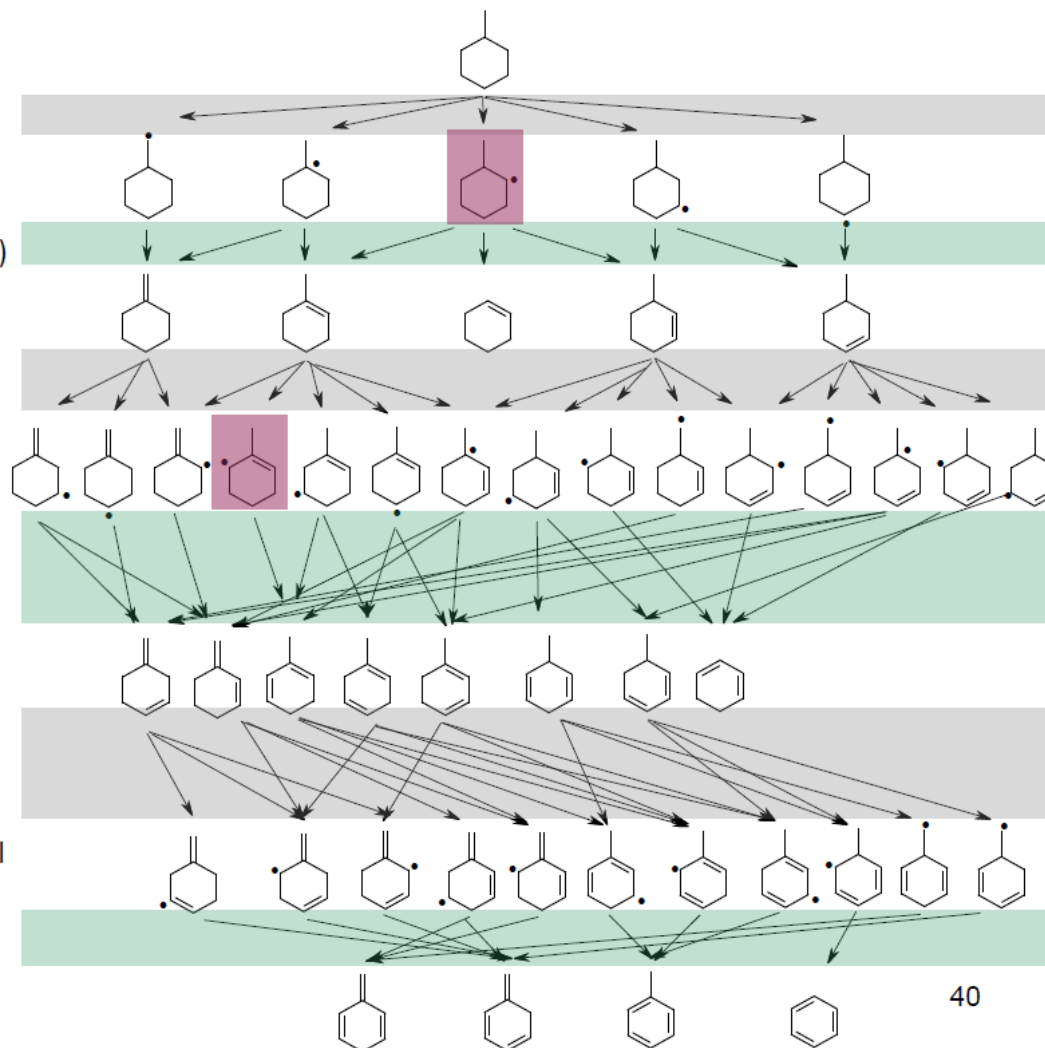
- H₂ eliminations
- H-shifting
- β-scission ring-openings

Total Submechanism:

~40 species

~150 reactions

Many intermediates with
nearly identical reaction
paths and thermochemical
properties.



The JetSurF Experience

Objective 1 – Qualitative Insights

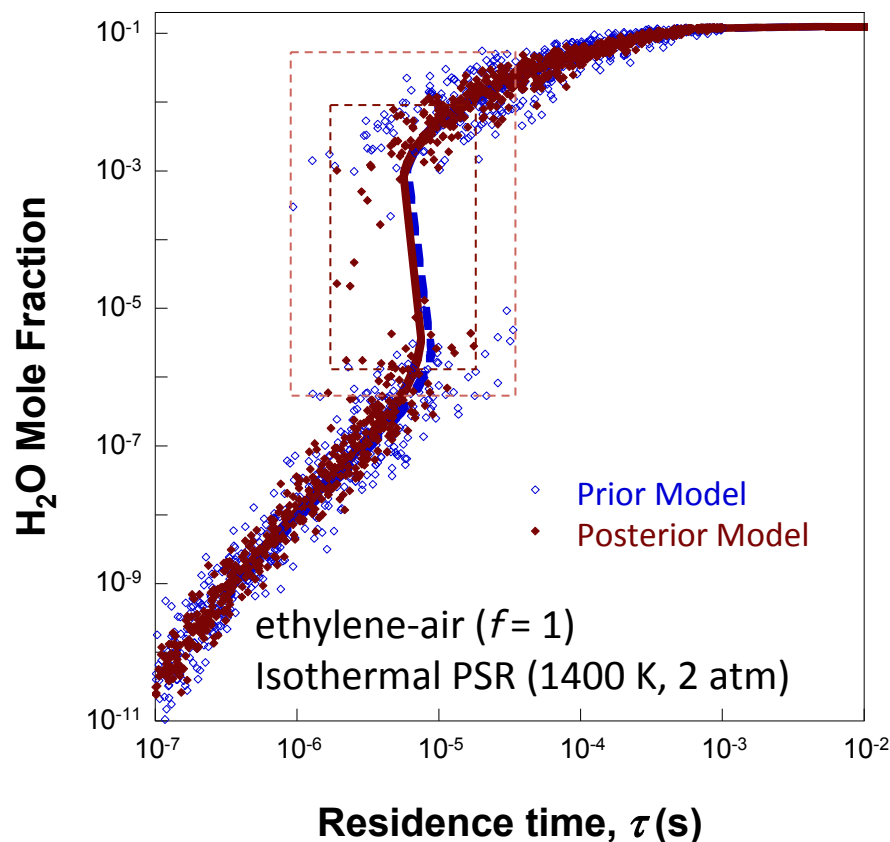
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The JetSurF Experience

- A severely under-defined mathematical problem.
 - unknown pathways/rates, inaccurate rate coefficients
- Even if reaction pathways are known and the problem can be treated as an inverse problem, we are still facing large uncertainties.



Sheen & Wang (2012)

The JetSurF Experience

Objective 1 – **Qualitative Insights**

- What chemistry causes faster ignition delay?
- Why a certain fuel propagates a flame faster than another?
- What does blending do to various combustion behaviors?
- What chemistry leads to increased low-T reactivity and why?
-

Objective 2 – **Quantitative Predictions** – in a surrogate approach

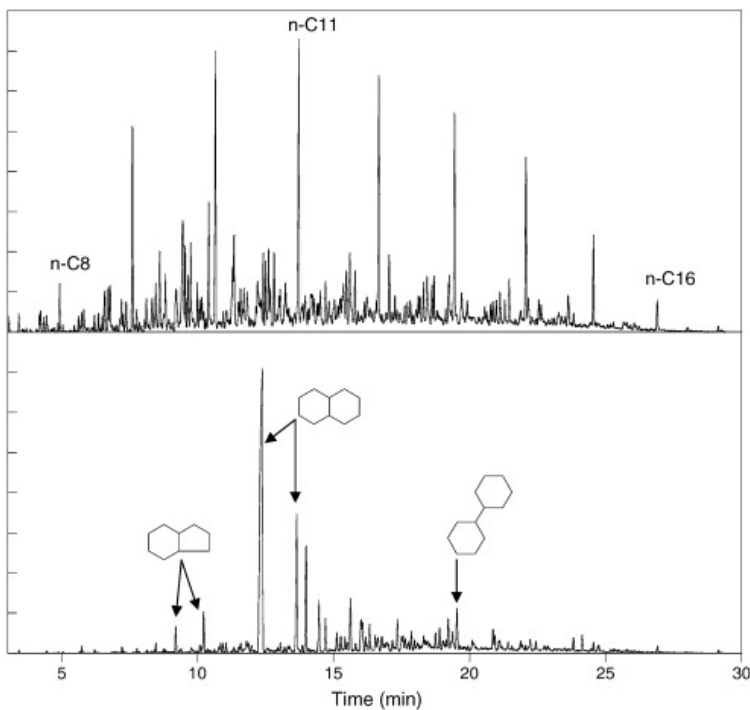
- > 95% reaction pathways/rates are assumed.
- Lumping/reaction class assumption falls apart for unimolecular and chemically activated reactions.
- Uncertainties in $k(T,p)$ are too large to pin predictions without tuning.
- Fundamentally an ill-defined mathematic problem – ab initio theories and uncertainty quantification can't address all of the issues at this time.
- Kinetic coupling – a large thermodynamic condition space: can we test it all?

Development of reaction kinetic model for large fuels is not an exact science. If we must rely on empiricism, what is the most logical path to predictability?

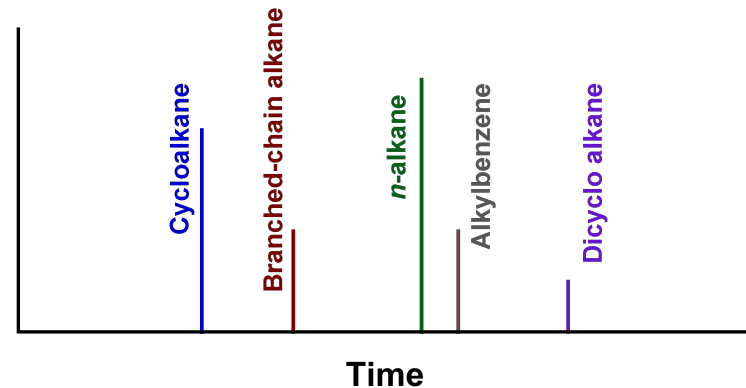
The Current Surrogate Approach

- **Key Assumptions:**

- A mixture of several neat hydrocarbons can mimic the chemical and physical behaviors of a real jet fuel – **lumping** at the fuel level.
 - *n*-dodecane, *n*-butylcyclohexane, dimethyloctane, *n*-propylbenzene, etc.



Lumping



A real fuel – thousands of compounds – combustion chemistry not tractable at a fundamental level.

A surrogate fuel – mimics a real fuel

- Physical properties
- Chemical properties
 - Enthalpy, C/H, chemical functionalities, combustion behaviors, ...
- Combustion chemistry models, in principle, tractable at a fundamental level

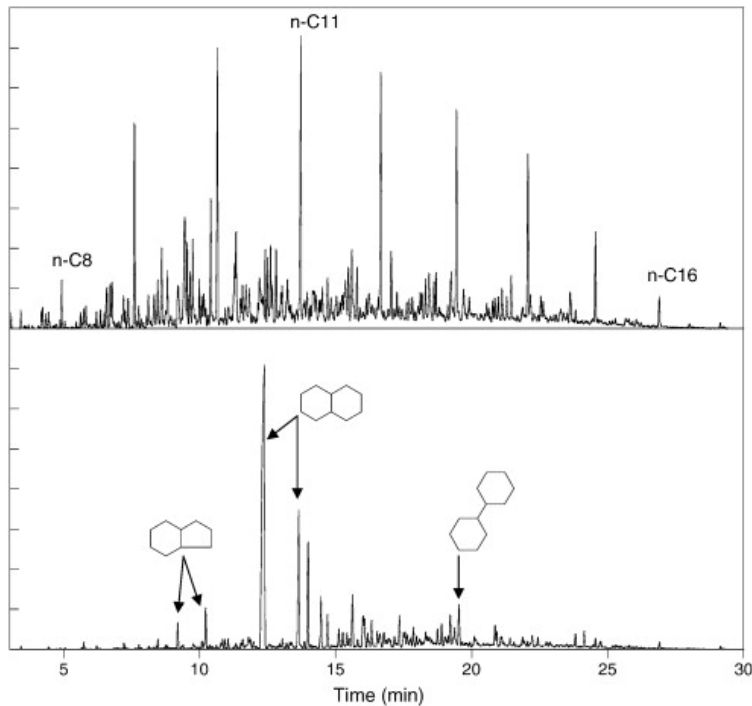
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- A mixture of several neat hydrocarbons can mimic the chemical and physical behaviors of a real jet fuel – **lumping** at the fuel level.
 - *n*-dodecane, *n*-butylcyclohexane, dimethyloctane, *n*-propylbenzene, etc.
- Detailed models for individual surrogate components can be developed and validated, rationally and thoroughly. It requires
 - An examination of assumptions involving all reaction pathways/rate coefficients;
 - Validation against a wide range of conditions encountered in turbulent flames, premixed and non-premixed.
- kinetic coupling of components and their reaction intermediates can be verified experimentally in an efficient manner.

- **For tools available, the current approach is semi-empirical in at least two aspects – the many assumptions made in the kinetic models and the approach to lumping itself.**

An Alternative Surrogate Approach



Map out flame
preheat
zone cracking
kinetics

$$x(T(t), p)$$

Detailed Model

C_2H_4 , H_2 , CH_4 , C_3H_6 , 1-
 C_4H_8 (+soot
precursors)

CO , CO_2 , H_2 , H_2O etc

A real fuel – thousands of compounds –
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An Alternative Surrogate Approach

- **Key assumptions:**

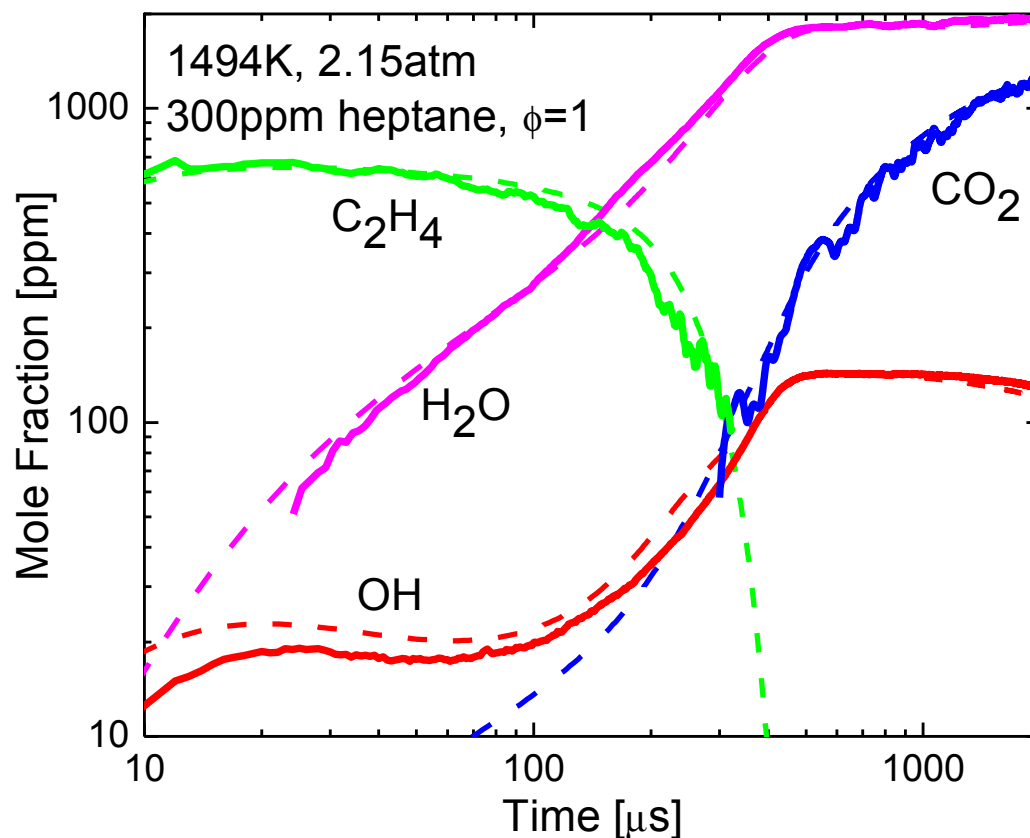
- Large fuels do not enter into the flame sheet directly. They must undergo cracking before oxidation;
- In the presence of a flame, the cracking kinetics is fast and may be decoupled from the oxidation kinetics of cracking products;
- The oxidation of the cracked products determine ultimately the rates of radical pool build-up and heat release.

- **Approach:**

- Seek to identify low-dimensional kinetic manifold(s) that describe(s) the kinetics of real fuel cracking directly, leading to a very limited number of smaller molecular fragments (H_2 , CH_4 , C_2H_4 , C_3H_6 , 1- C_4H_8 , C_6H_6 etc.). *The rates don't matter as much as the composition of the cracking products.*
- Detailed kinetic description of $\text{H}_2/\text{C}_1\text{-C}_4$ pyrolysis and oxidation reaction kinetics.

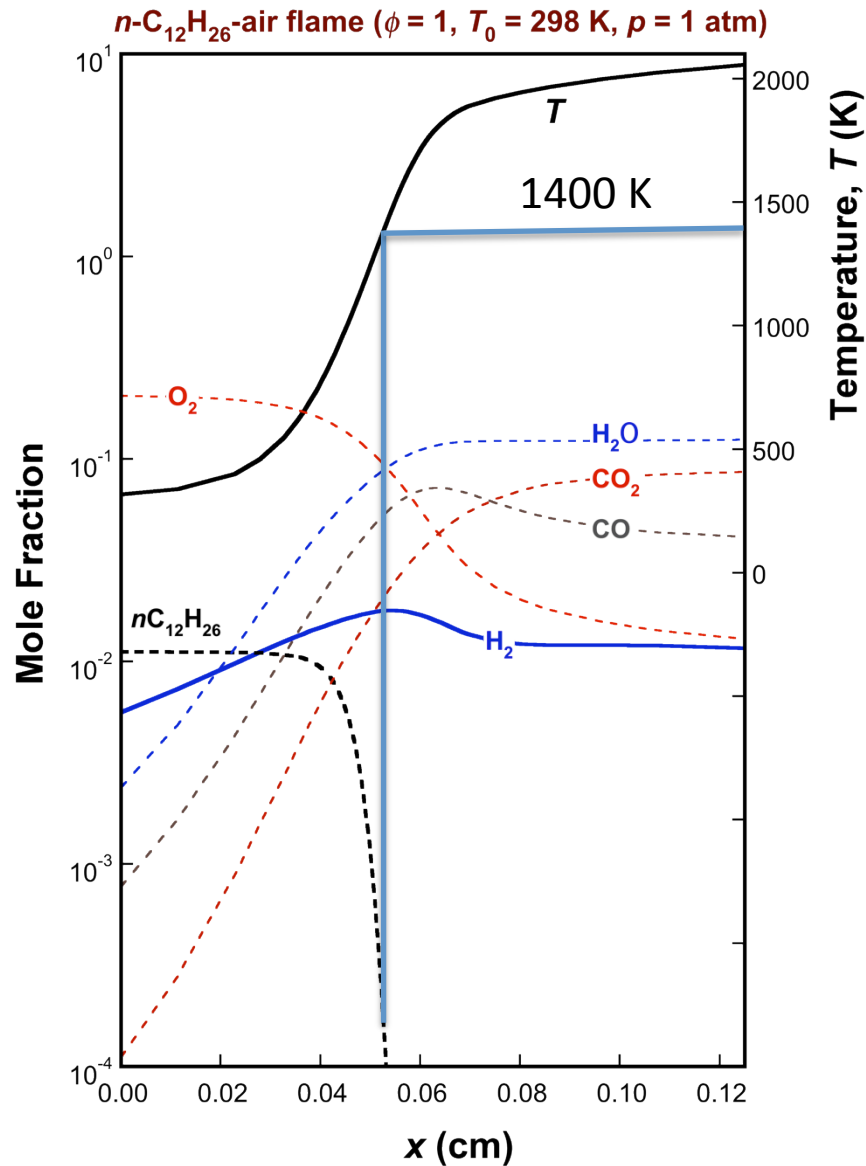
Chemistry in Homogeneous Reactor and Laminar Flames

- Large fuel molecules cracks into small fragments (H_2 , CH_4 , C_2H_4 , C_3H_6 etc) initially over a substantially short time period before oxidation dominated by radical-chain branching.



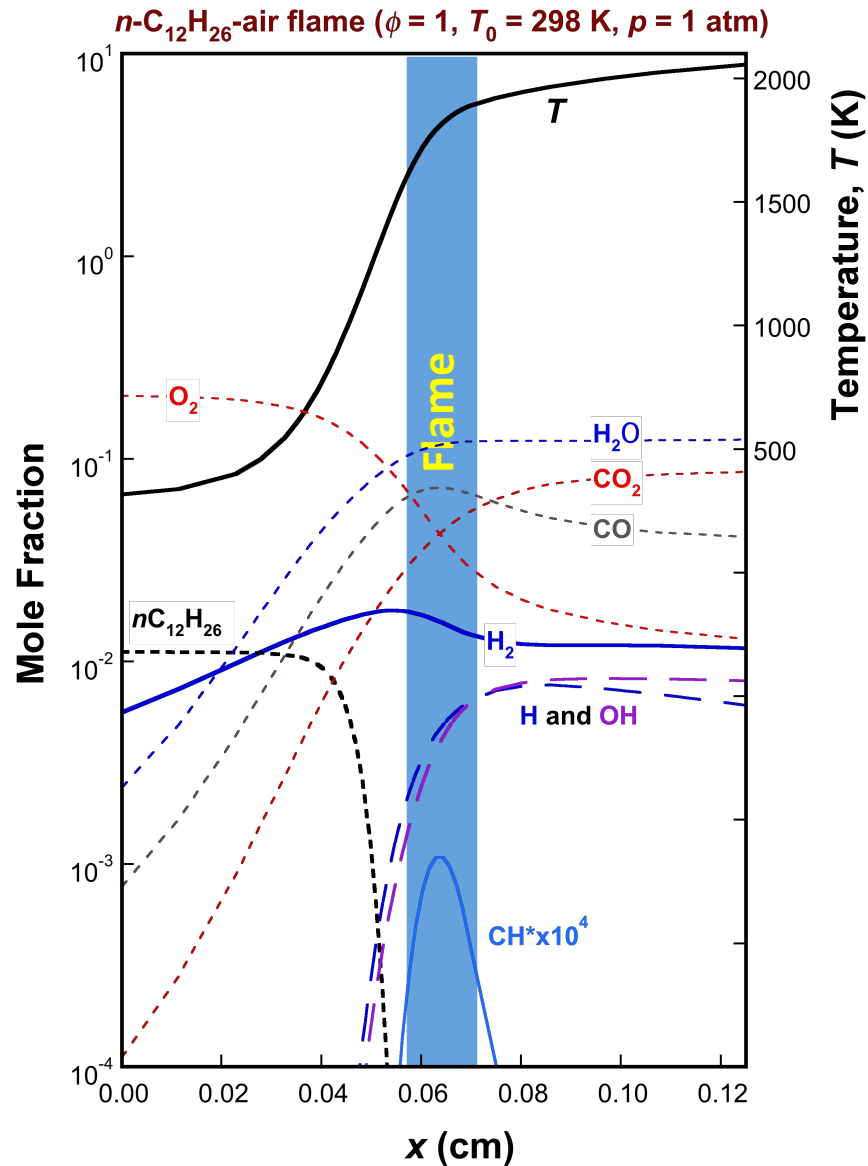
Davidson, Hong, Pilla, Farooq, Cook & Hanson, *Combustion and Flame* (2010)

Laminar Flame Structure and Fuel Kinetics



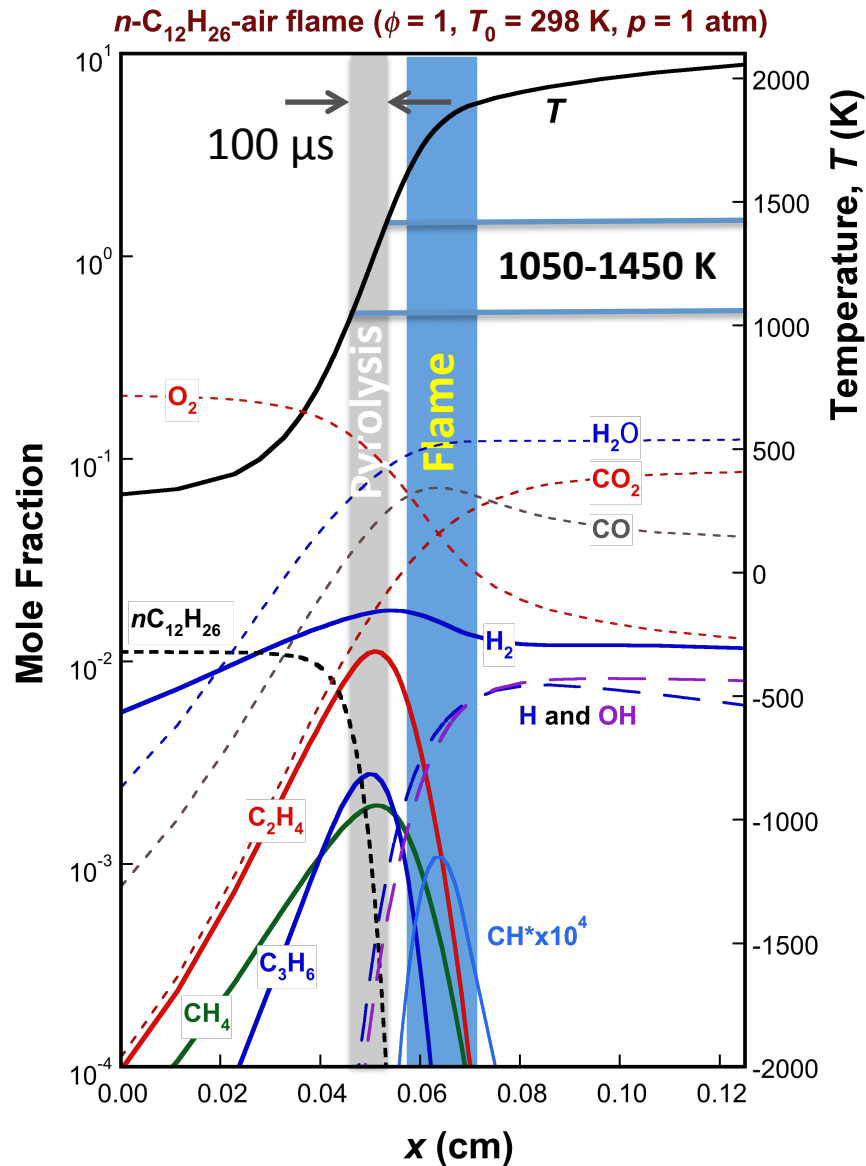
- Fuel takes a nose-dive before oxygen is depleted.
- The temperature at which dodecane is depleted is 1400 K.

Laminar Flame Structure and Fuel Kinetics



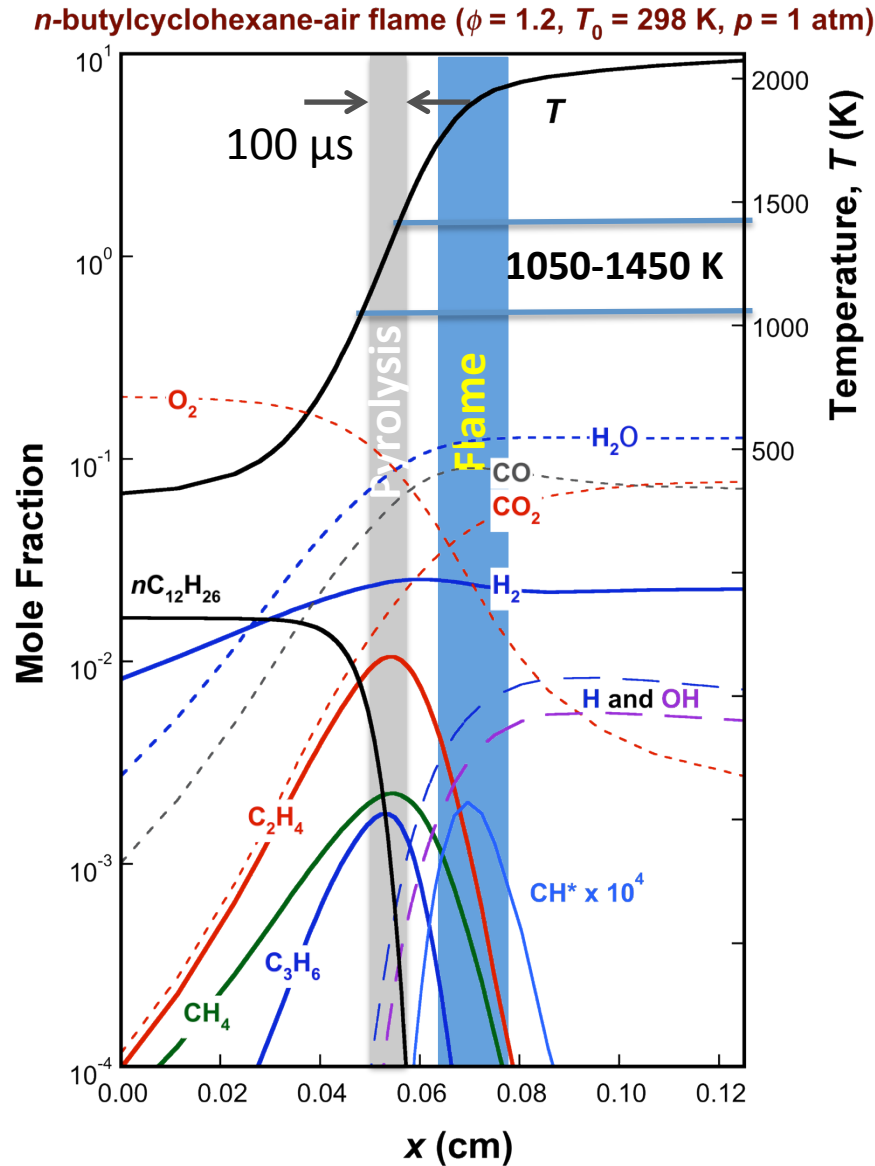
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- Flame is established after the parent fuel is gone.
- The parent fuel cracks to C_2H_4 , C_3H_6 , CH_4 and H_2 which enter into the flame, is oxidized and release heat.
- The pyrolysis zone is separated from the flame.
- Pyrolysis occurs in the $\sim 1000\text{--}1450\text{ K}$ window and is facilitated by H and OH (10^{-4} to 10^{-3} in mole fractions).
- Pyrolysis took $\sim 100\ \mu\text{s}$.

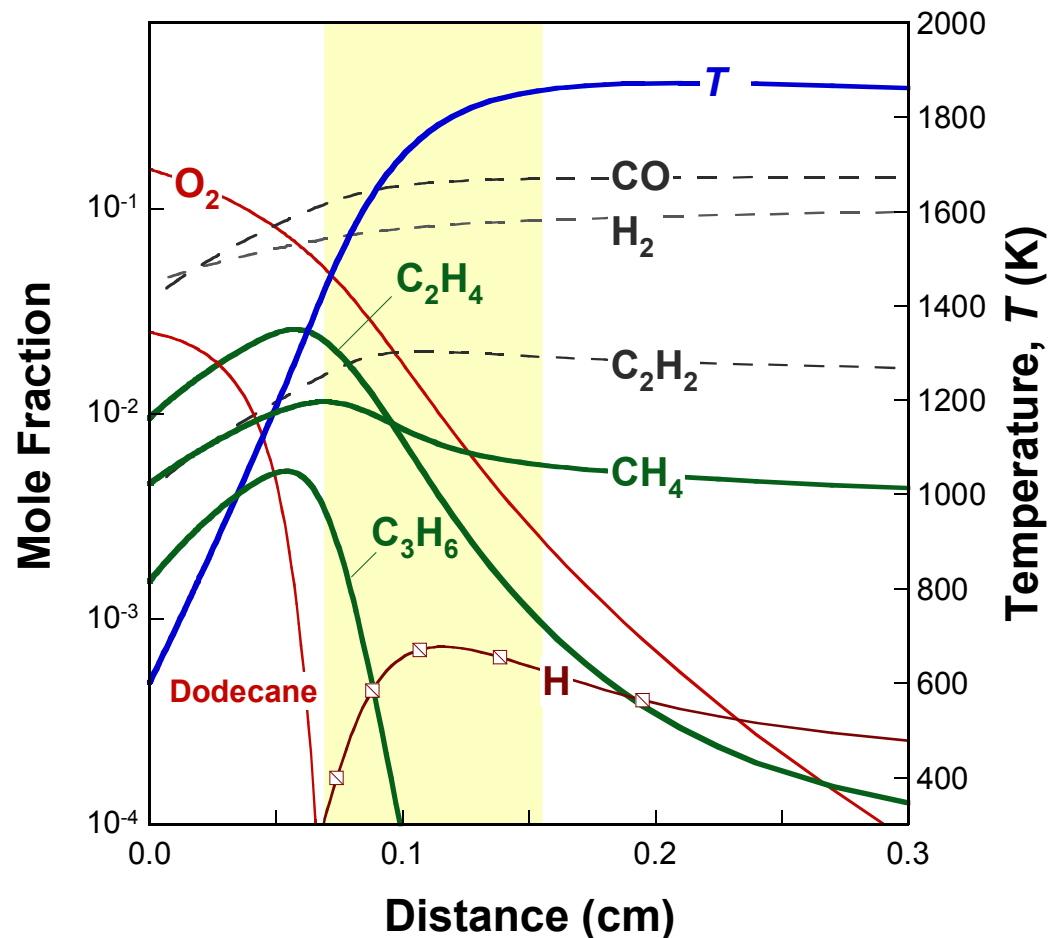
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- Pyrolysis occurs in the 1050-1450 K window and is facilitated by H and OH (10^{-4} to 10^{-3} in mole fractions).
- Pyrolysis took $\sim 100 \mu$ s.
- Other fuels do not behave differently (except for aromatics).

Chemistry in Fuel Rich Flames

- In laminar flames, large fuel molecules cracks into small fragments in the preheat zone;
- Heat conducted from the flame is partitioned into sensible heat and reaction enthalpy (endothermicity due to fuel cracking);

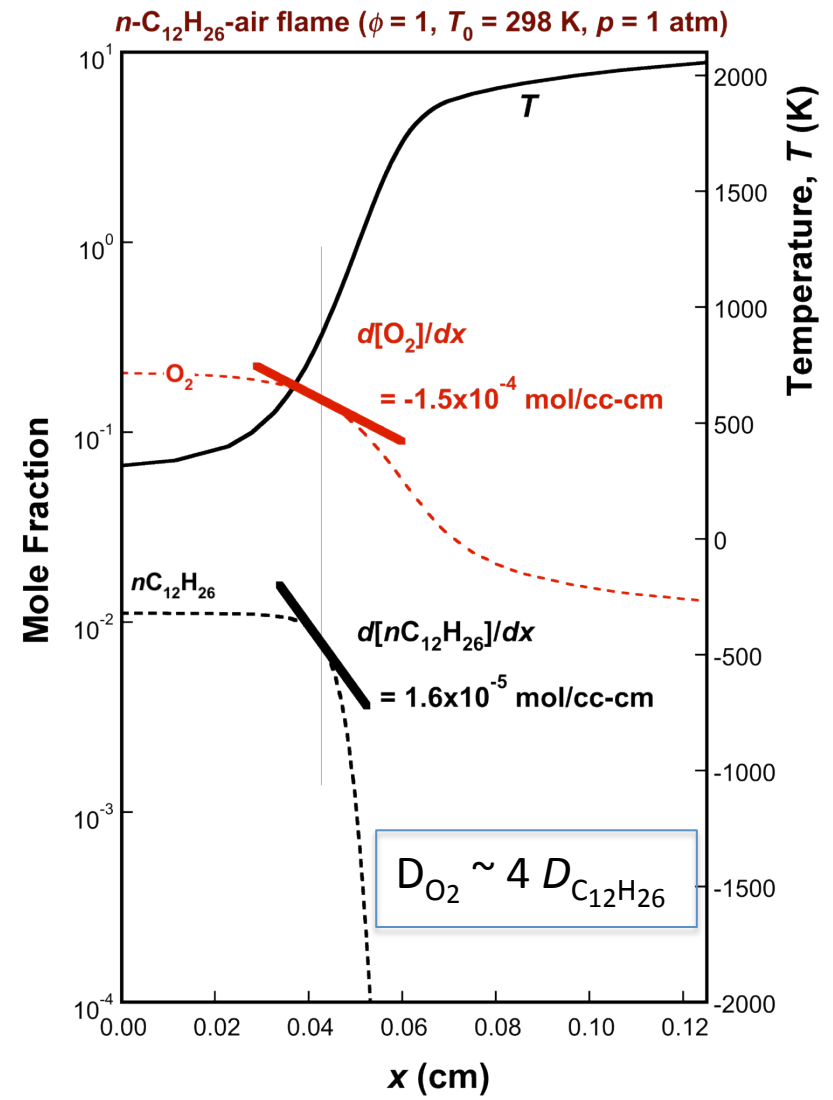


Lightly stretched burner-stabilized dodecane- O_2 -Ar flame ($\phi = 2.0$, 1 atm)

Abid et al. (2009)

Why Large Fuel Molecules and Flame Do Not Mix?

- Disparity in molecular diffusion rates
 - w/o cracking to smaller molecular fragments, the fuel would never have caught up with O_2 .



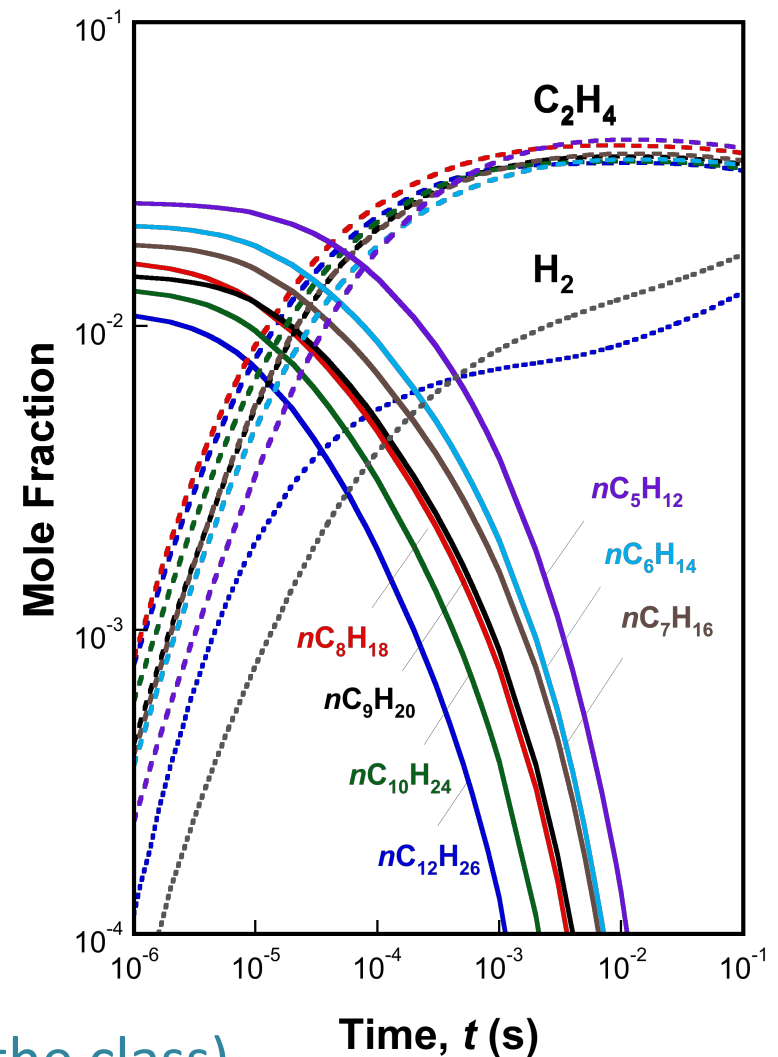
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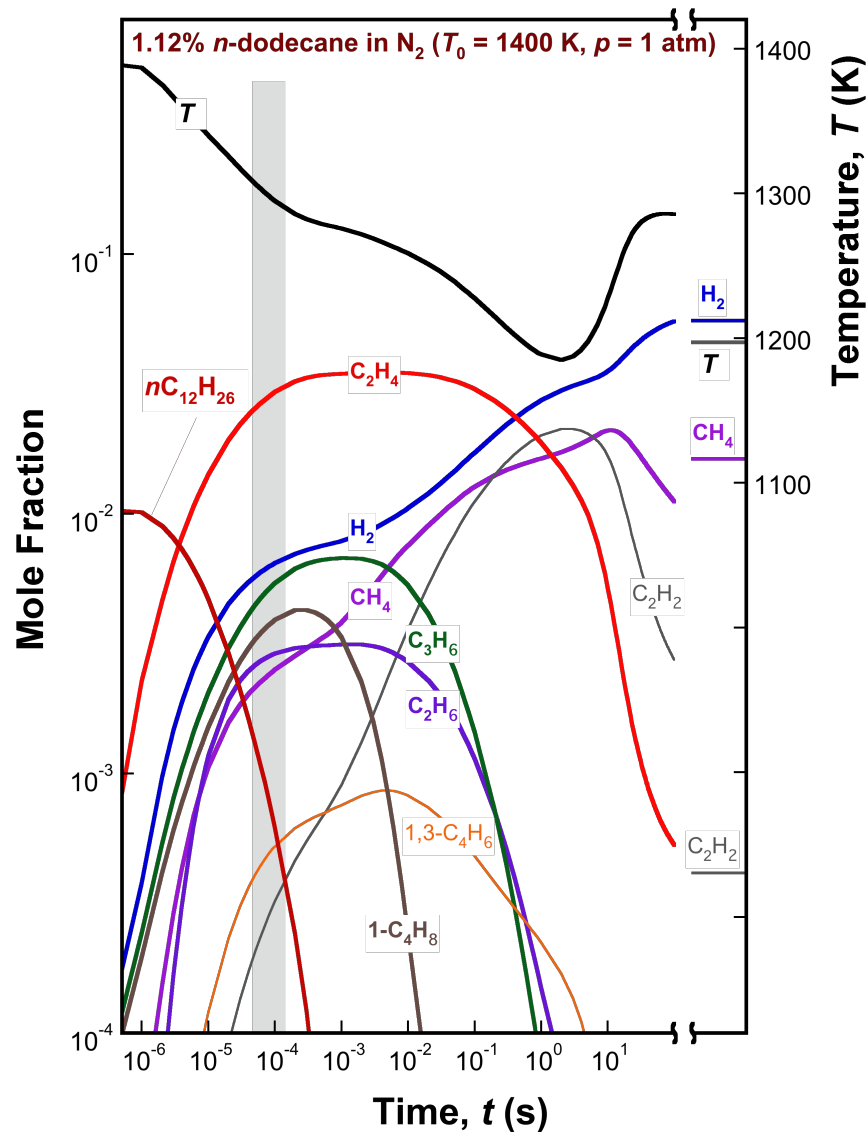
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- If the fuel and flame mix, cracking endothermicity would lower the local temperature, reduce heat conduction, and weaken the flame. Flame must move downstream to separate it from the fuel cracking zone.
- Large hydrocarbon fuels cracks faster than small hydrocarbons.
- Composition of cracked products insensitive to the size of the fuel (with the class)

Fuel Pyrolysis ($T_0 = 1350$ K, $p = 1$ atm,
 $[C] = 1.2 \times 10^{-6}$ mol/cc)

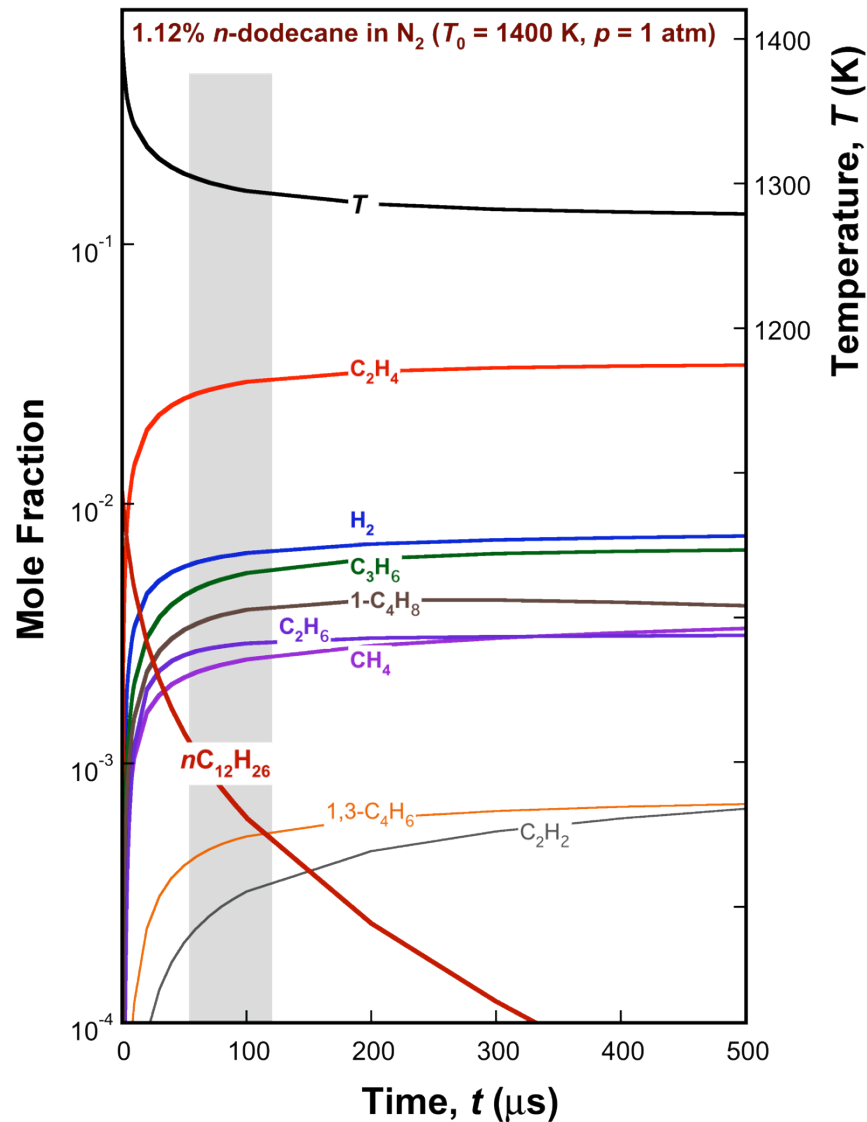


Homogeneous Cracking Kinetics



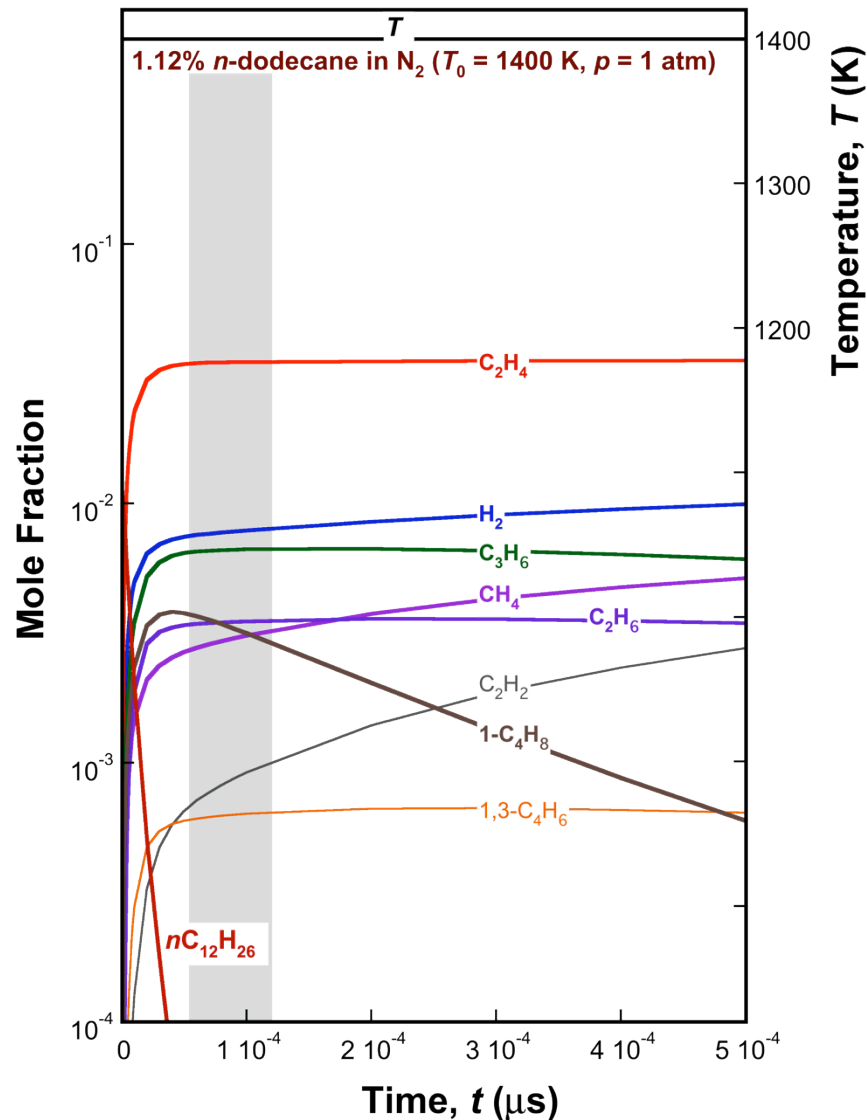
- Fuel cracking is endothermic and driven by entropy.
- For time scales relevant to flames
 - fuel cracking is kinetically controlled far from chemical equilibrium.
 - For *n*-alkanes, dominant products are C_2H_4 , H_2 , C_3H_6 , CH_4 , C_2H_6 and $1-C_4H_8$ (true for all *n*-alkanes).

Homogeneous Cracking Kinetics



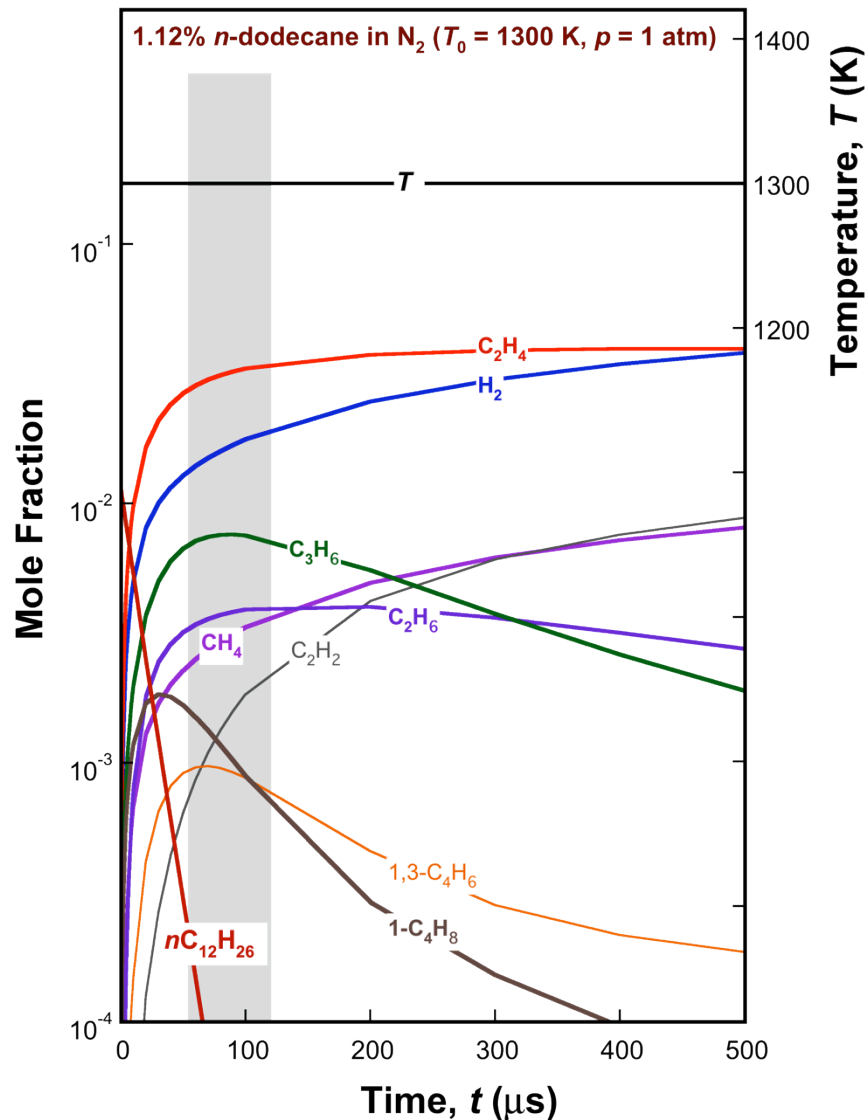
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- At the upper end of flame pyrolysis zone (~ 1400 K), pyrolysis reaches the “plateau” region within 100μ s without initial H and OH presence.

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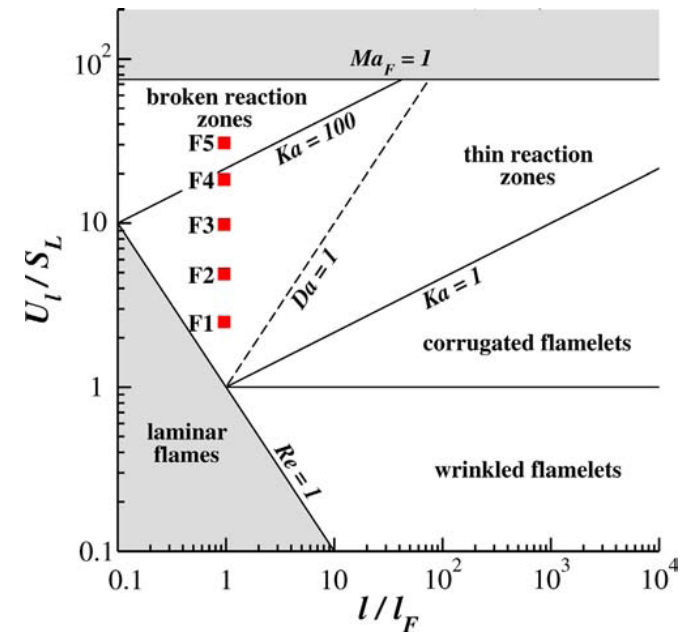
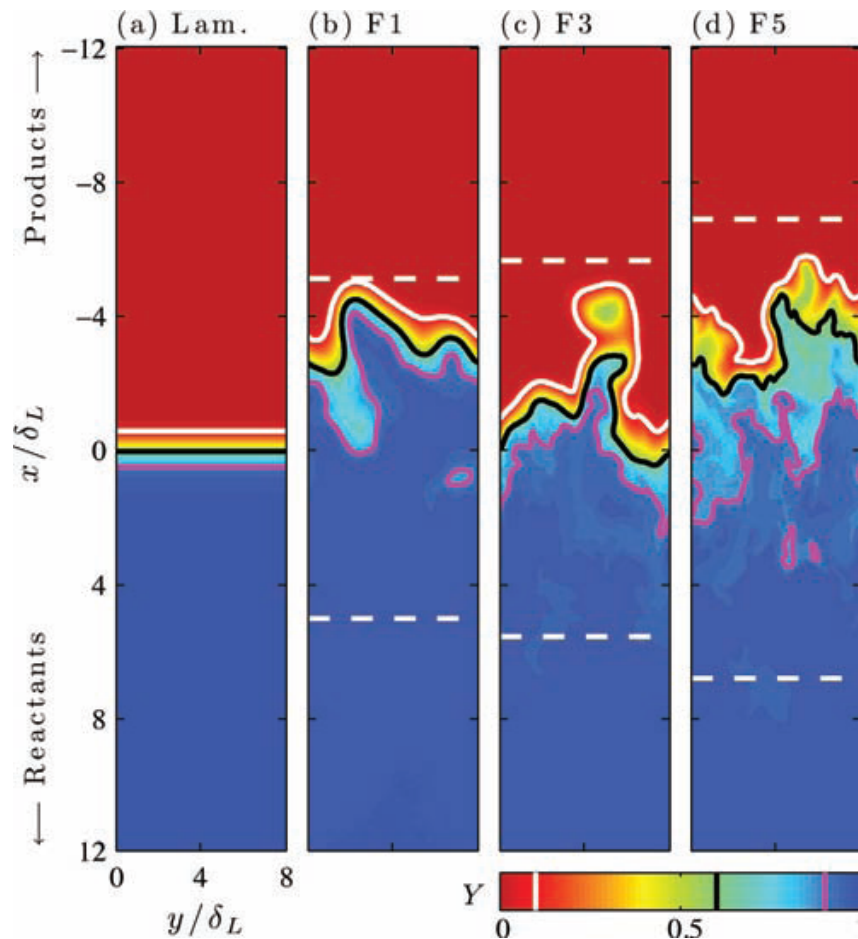
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Homogeneous Cracking Kinetics



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- At the upper end of flame pyrolysis zone (~ 1400 K), pyrolysis reaches the “plateau” region within $100 \mu s$ without initial H and OH presence.
- Cracking goes faster isothermally.
- It goes blazingly faster when radicals are brought in (100 PPM H atom) – reaching the plateau within $< 100 \mu s$ at 1300 K.

Turbulence Can Enhance Fuel Cracking Rates



Simulation	Reaction zone (δ_L) ($0.1 < Y < 0.6$)	Preheat zone (δ_L) ($0.6 < Y < 0.9$)	Flame brush $\bar{\delta}_T/\delta_L$
F1	0.60	0.61	12.1
F2	0.64	0.83	12.5
F3	0.71	1.2	13.6
F4	0.84	1.4	14.5
F5	0.91	1.7	15.7

An Alternative Surrogate Approach

- **Key assumptions:**

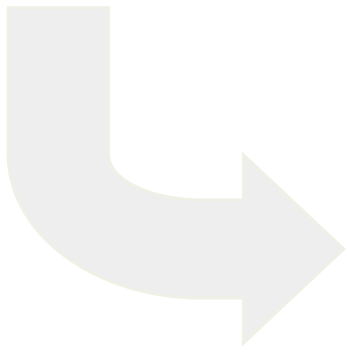
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Alternative Surrogate Approach – A Feasibility Study

With Egolfopoulos



1. Test the concept on *n*-dodecane – develop a lumped model for *n*-dodecane pyrolysis.
2. Develop an empirical jet fuel cracking kinetic model from experiments.

(1) Test the Idea Against *n*-Dodecane

Lumped Model of *n*-Dodecane

No.	Reaction	<i>A</i>	<i>n</i>	<i>E_a</i>
1	$n\text{-C}_{12}\text{H}_{26} \rightarrow 3\text{C}_2\text{H}_4 + 2n\text{-C}_3\text{H}_7$	5.6×10^{26}	-2.7	88171
2	$n\text{-C}_{12}\text{H}_{26} \rightarrow 2\text{C}_2\text{H}_4 + 2p\text{-C}_4\text{H}_9$	5.1×10^{25}	-2.5	88117
3	$n\text{-C}_{12}\text{H}_{26} + \text{H} \rightarrow 4\text{C}_2\text{H}_4 + p\text{-C}_4\text{H}_9 + \text{H}_2$	1.3×10^6	2.5	6756
4	$n\text{-C}_{12}\text{H}_{26} + \text{H} \rightarrow 1.2\text{C}_2\text{H}_4 + 0.2\text{C}_3\text{H}_6 + 0.4n\text{-C}_3\text{H}_7 + 0.2\text{C}_4\text{H}_8 - 1 + 0.6p\text{-C}_4\text{H}_9 + 0.2\text{C}_5\text{H}_{10} + 0.6\text{C}_6\text{H}_{12} + \text{H}_2$	1.3×10^6	2.4	4471
5	$n\text{-C}_{12}\text{H}_{26} + \text{O} \rightarrow 4\text{C}_2\text{H}_4 + 2p\text{-C}_4\text{H}_9 + \text{OH}$	1.9×10^5	2.7	3716
6	$n\text{-C}_{12}\text{H}_{26} + \text{O} \rightarrow 1.2\text{C}_2\text{H}_4 + 0.2\text{C}_3\text{H}_6 + 0.4n\text{-C}_3\text{H}_7 + 0.2\text{C}_4\text{H}_8 - 1 + 0.6p\text{-C}_4\text{H}_9 + 0.2\text{C}_5\text{H}_{10} + 0.6\text{C}_6\text{H}_{12} + \text{OH}$	4.8×10^4	2.7	2106
7	$n\text{-C}_{12}\text{H}_{26} + \text{OH} \rightarrow 4\text{C}_2\text{H}_4 + 2p\text{-C}_4\text{H}_9 + \text{H}_2\text{O}$	1.4×10^3	2.7	527
8	$n\text{-C}_{12}\text{H}_{26} + \text{OH} \rightarrow 1.2\text{C}_2\text{H}_4 + 0.2\text{C}_3\text{H}_6 + 0.4n\text{-C}_3\text{H}_7 + 0.2\text{C}_4\text{H}_8 - 1 + 0.6p\text{-C}_4\text{H}_9 + 0.2\text{C}_5\text{H}_{10} + 0.6\text{C}_6\text{H}_{12} + \text{H}_2\text{O}$	2.7×10^4	2.4	393
9	$n\text{-C}_{12}\text{H}_{26} + \text{CH}_3 \rightarrow 4\text{C}_2\text{H}_4 + 2p\text{-C}_4\text{H}_9 + \text{CH}_4$	1.8	3.7	7153
10	$n\text{-C}_{12}\text{H}_{26} + \text{CH}_3 \rightarrow 1.2\text{C}_2\text{H}_4 + 0.2\text{C}_3\text{H}_6 + 0.4n\text{-C}_3\text{H}_7 + 0.2\text{C}_4\text{H}_8 - 1 + 0.6p\text{-C}_4\text{H}_9 + 0.2\text{C}_5\text{H}_{10} + 0.6\text{C}_6\text{H}_{12} + \text{CH}_4$	3.0	3.5	5480

C-C fissions

H-abstraction

+

β-scissions

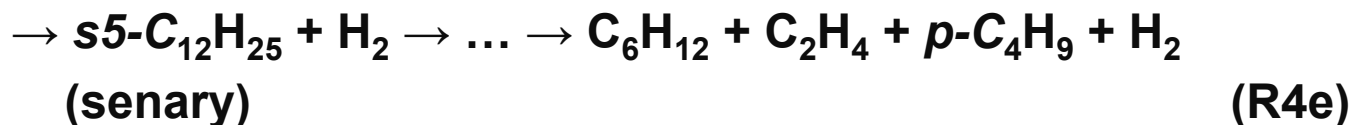
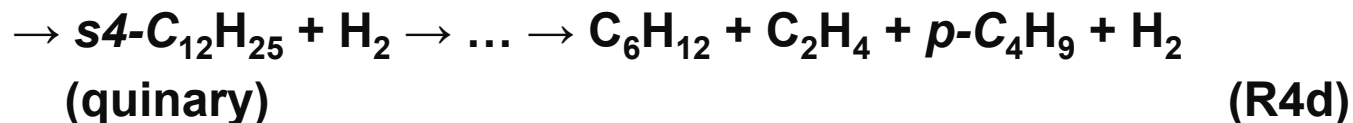
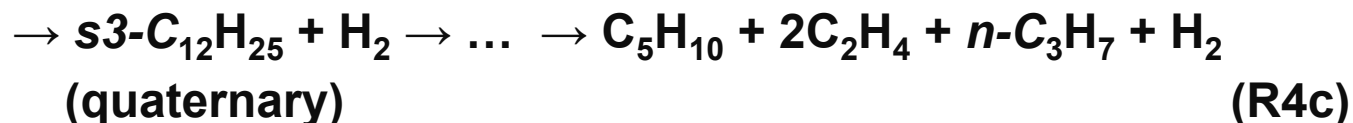
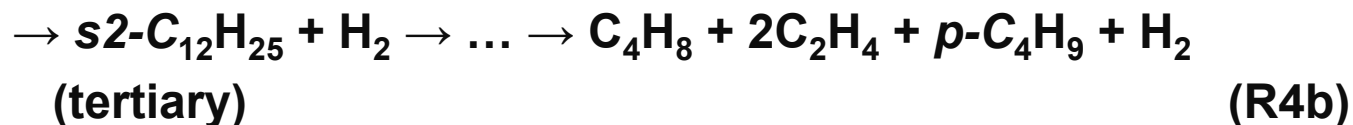
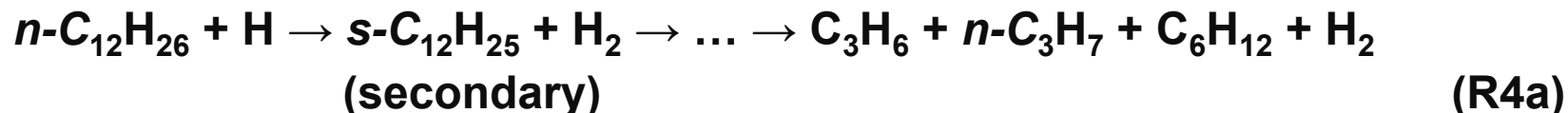
Units are mol, cm, sec, Cal, and K.

You et al. 2009

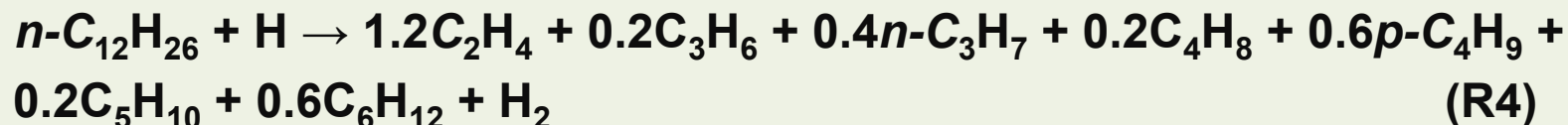
(1) Test the Idea Against *n*-Dodecane

Lumped Model of *n*-Dodecane

For example:

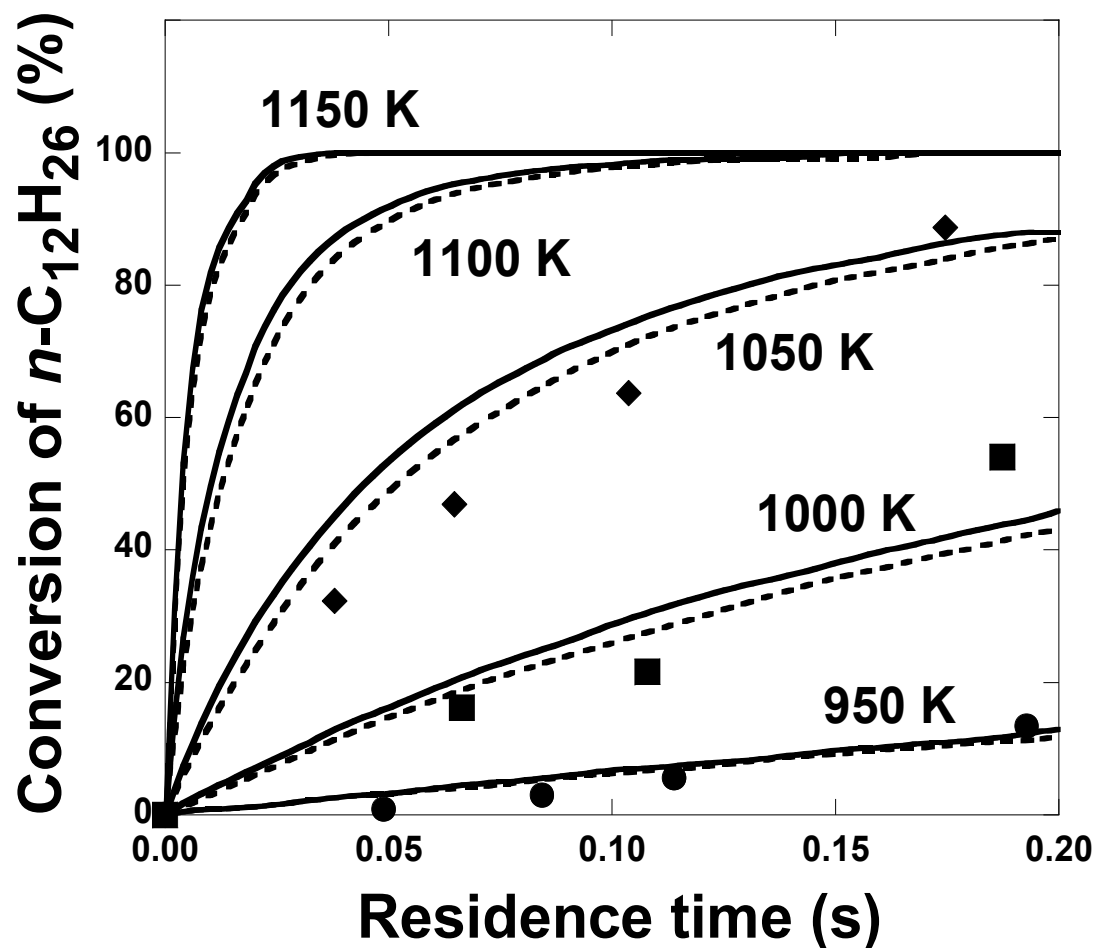


A lumped step by assuming the rates of H-abstraction to be identical



(1) Test the Idea Against *n*-Dodecane – Selected Results

n-C₁₂H₂₆ pyrolysis in a plug flow reactor (0.336% *n*-C₁₂H₂₆-N₂, *p* = 1 atm)

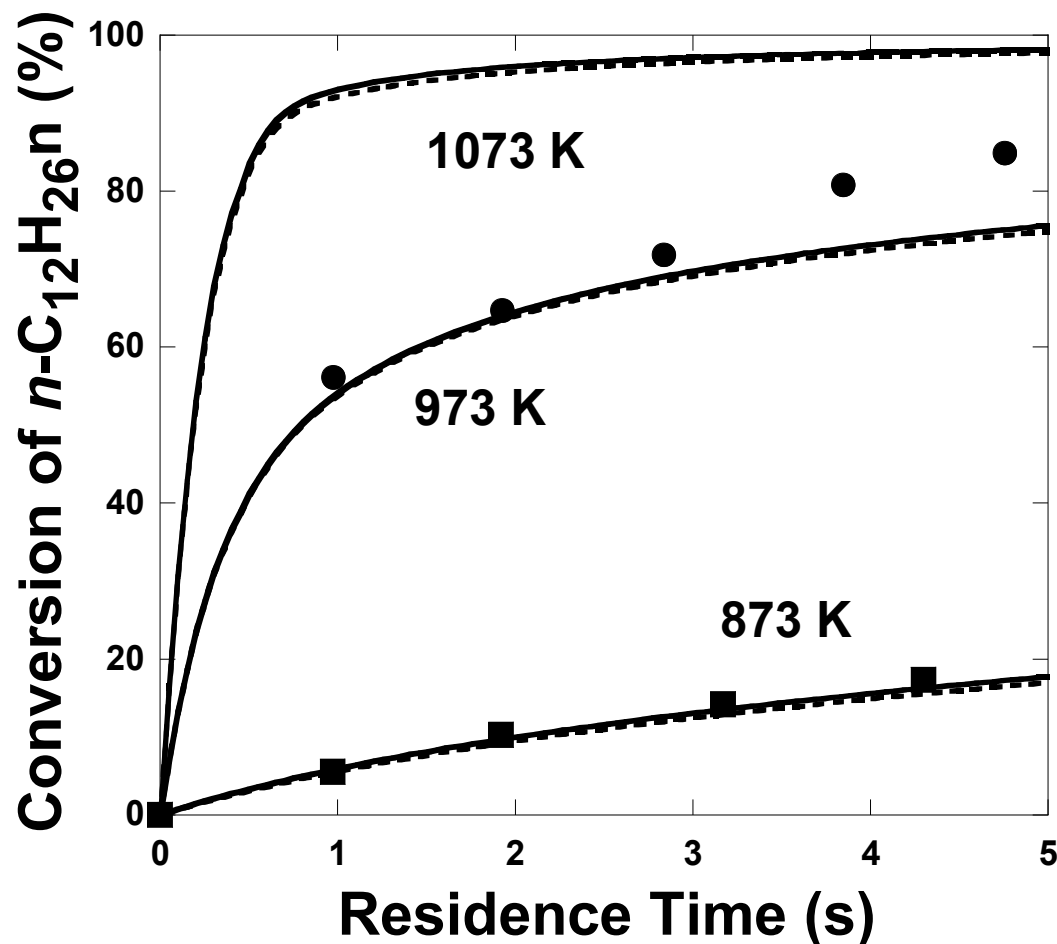


Experimental data: Dahm et al.; Solid lines: detailed model; dashed line: lumped C₁₂ model + USC Mech II

You et al. 2009

(1) Test the Idea Against n-Dodecane – Selected Results

2% $n\text{-C}_{12}\text{H}_{26}$ pyrolysis in He in a jet-stirred reactor ($p = 1$ atm)

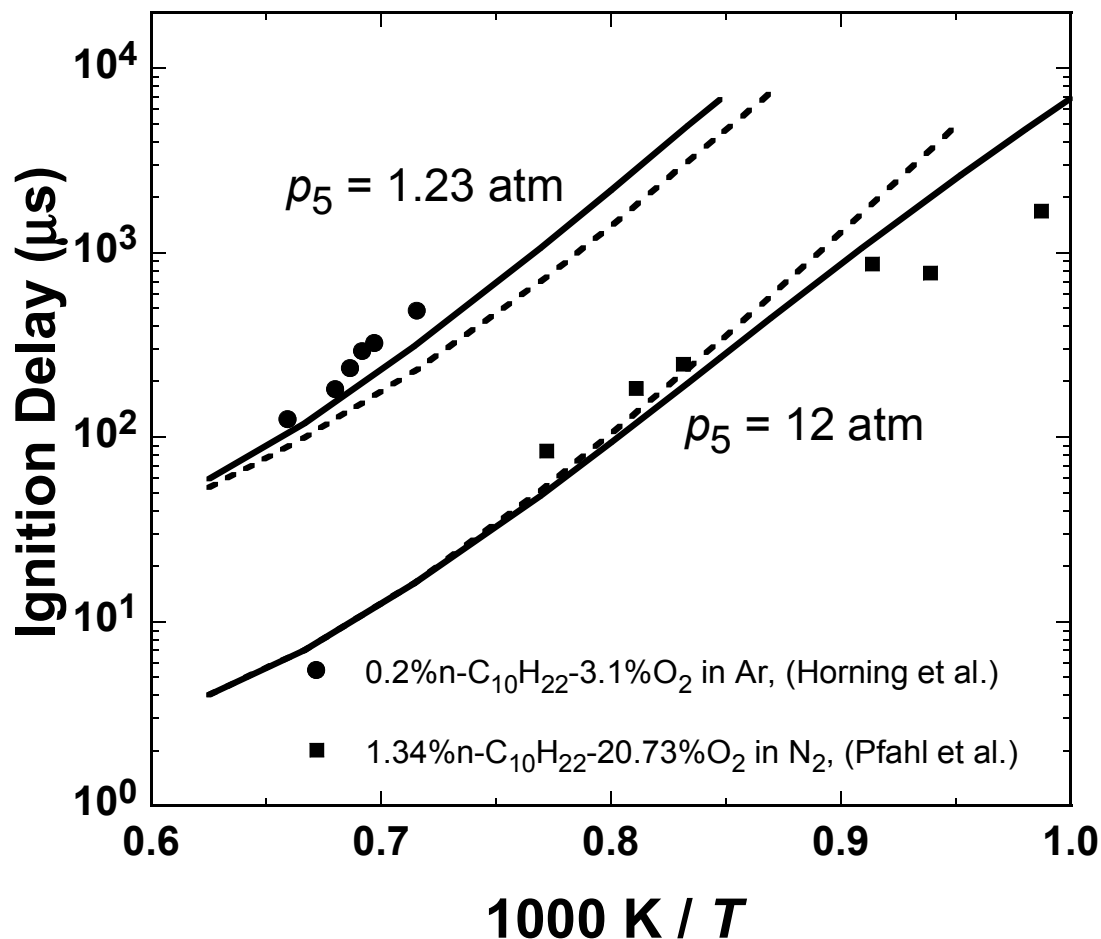


Experimental data: Herbinet et al.; Solid lines: detailed model;
dashed line: lumped C_{12} model + USC Mech II

You et al. 2009

(1) Test the Idea Against *n*-Dodecane – Selected Results

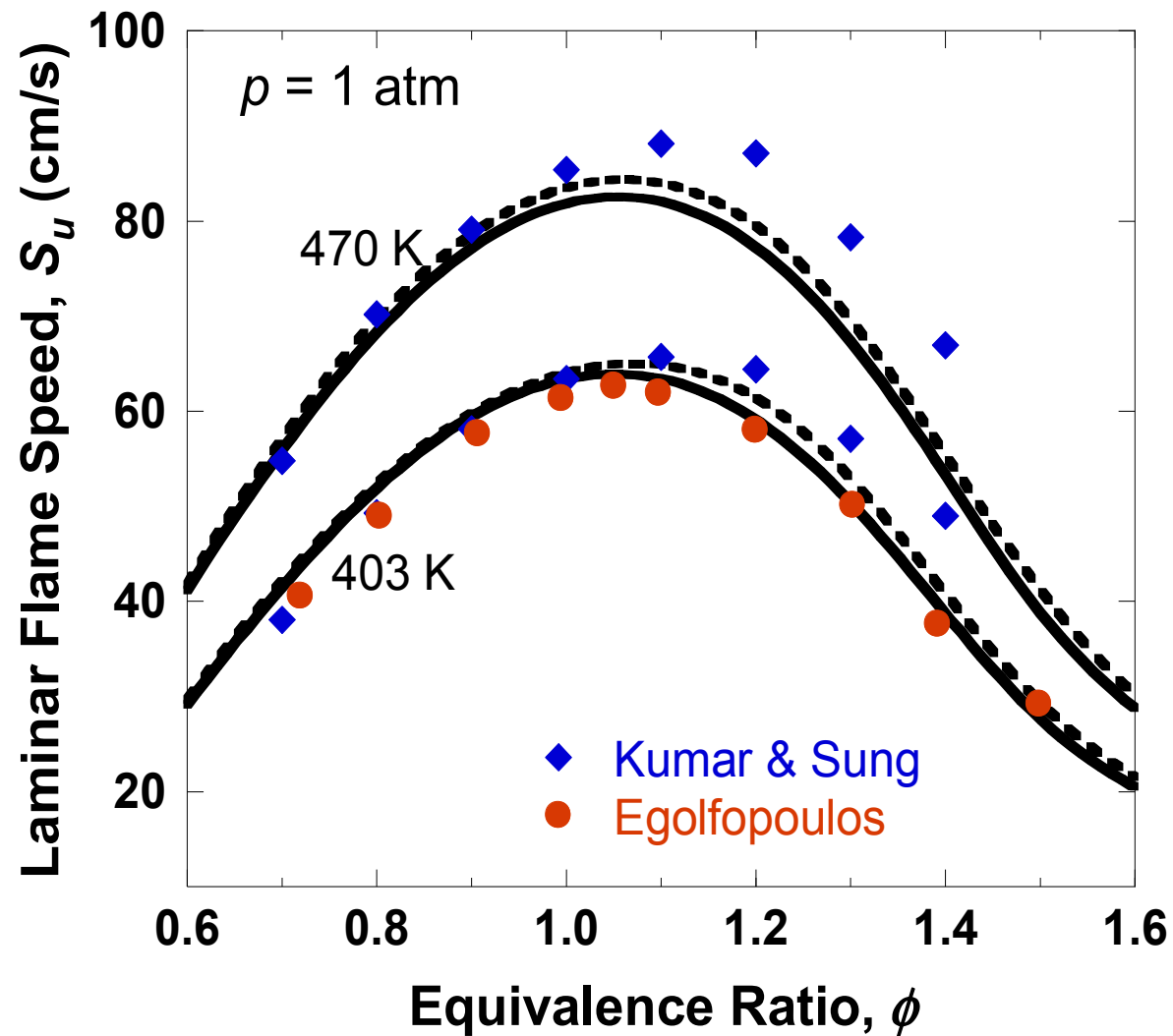
n-C₁₀H₂₂ oxidation behind reflected shock waves



Experimental data: Herbinet et al.; Solid lines: detailed model; dashed line: lumped C₅-C₁₂ model + USC Mech II

(1) Test the Idea Against *n*-Dodecane – Selected Results

Laminar Flame Speed of *n*-Dodecane-Air Mixtures



Solid lines: detailed model; dashed line: lumped C_{12} model + USC Mech II

(1) Test the Idea Against *n*-Dodecane – Conclusions

- Fuel cracking and oxidation of cracked products (C_1 - C_4) are decoupled during high-temperature oxidation of *n*-dodecane.
- The same decoupling is expected to work for JP7, i.e., the reaction model may be approximated by a semi-empirical description of the cracking kinetics + a foundational fuel ($H_2/CO/C_1$ - C_4) model.

(2) Test the Idea Against JP7 – Cracking Model

The cracking model tuned against turbulent flow reactor experiments at 1 atm (residence time = 0.75 sec)

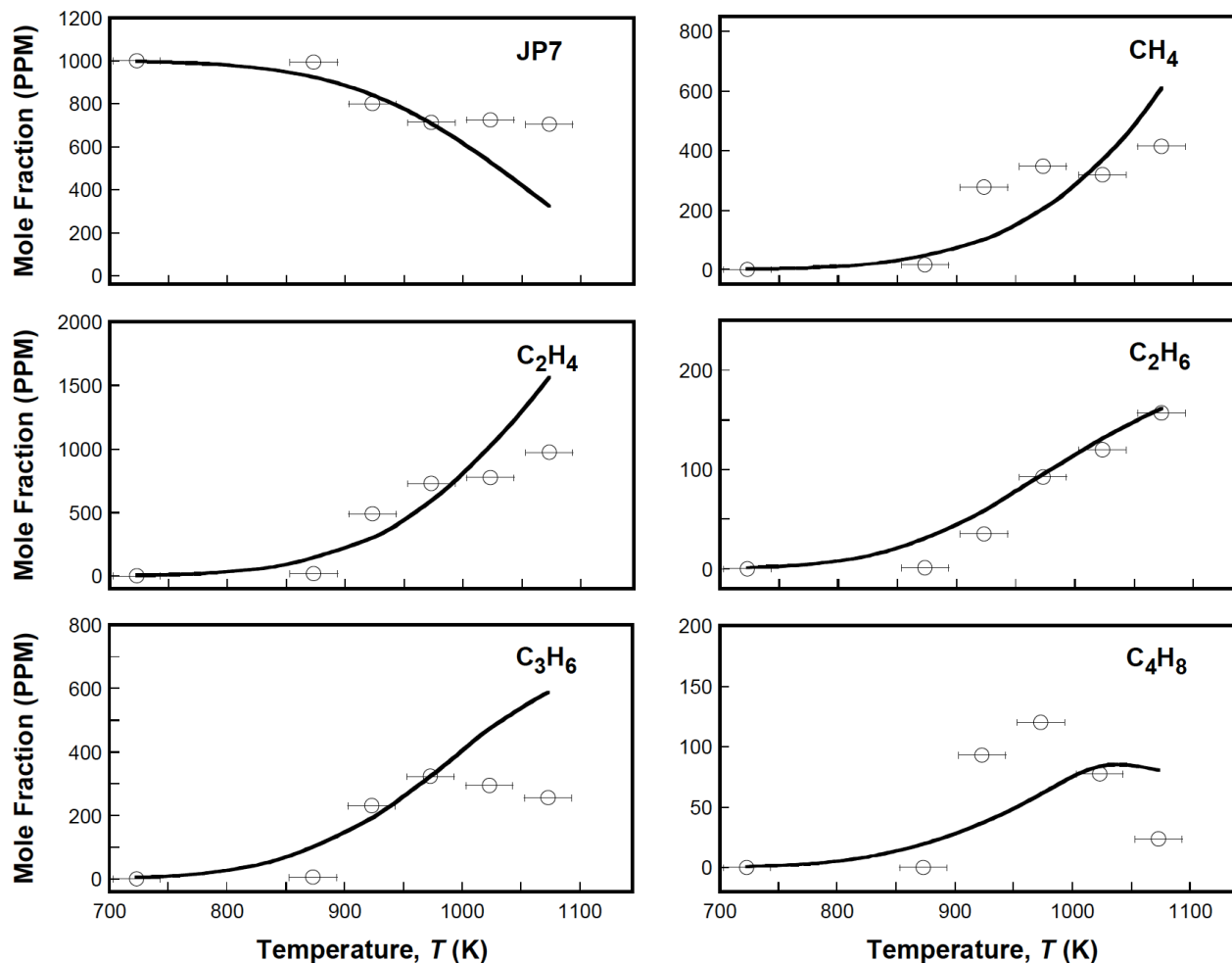


Figure 2. Experimental (symbols) and computed (lines) concentrations of species during JP7 pyrolysis in a turbulent flow reactor (0.1%-mol JP7 in N₂) at a residence time of 0.75 sec and a constant pressure of 1 atm, as a function of temperature. The experimental data of JP7 were derived from carbon balance. Simulations used the semiempirical JP7 model developed in the present work.

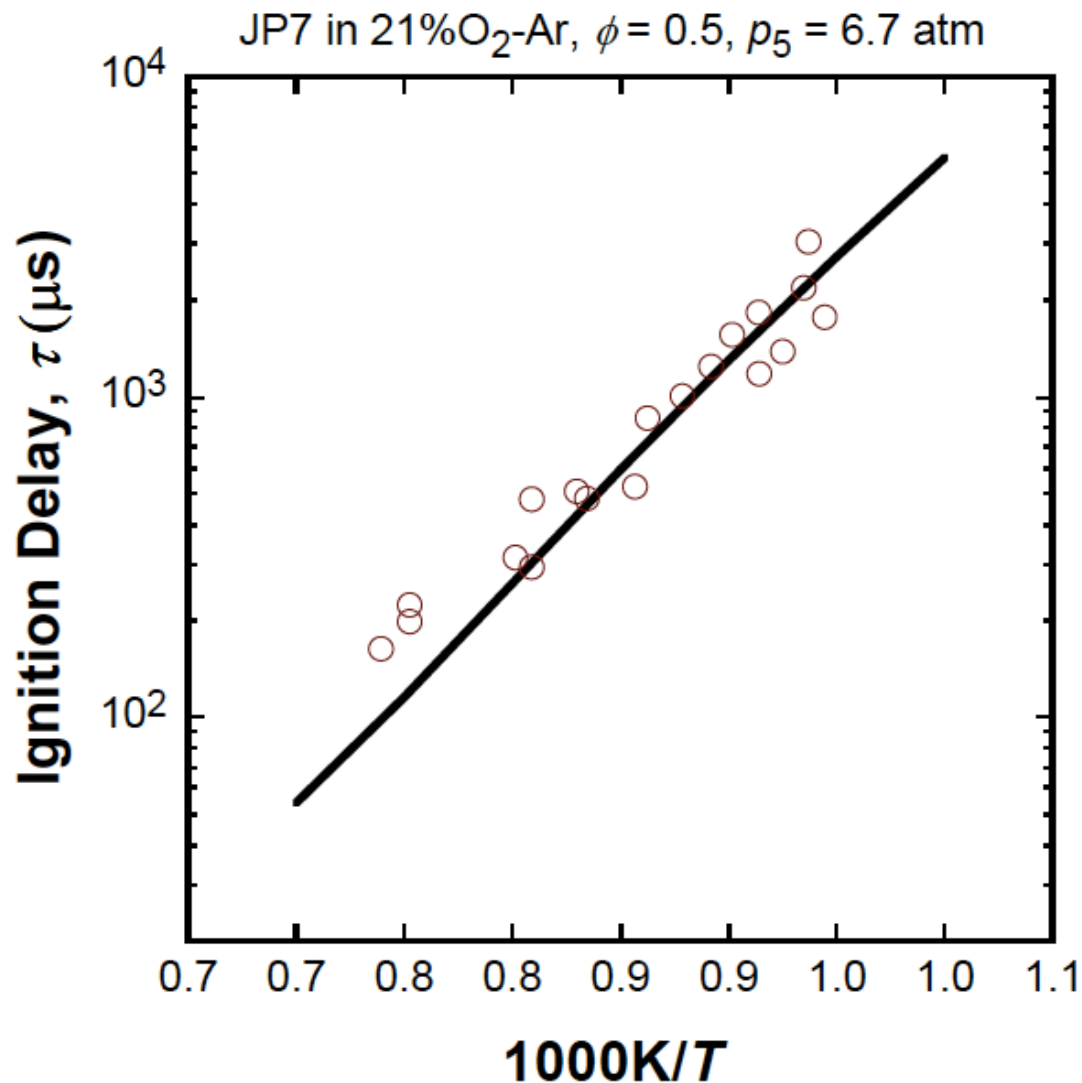
(2) Test the Idea Against JP7 – Cracking Model

Table 1. An Empirical JP7 Cracking Model^a

No.	Reaction	$k = A T^n e^{-E/RT}$		
		A	n	E
1	JP7 + M \rightarrow CH ₄ + 2C ₂ H ₄ + C ₃ H ₆ + C ₄ H ₇ + M	1.0 \times 10 ¹¹		30000
2	JP7 + H \rightarrow CH ₃ + 2C ₂ H ₄ + C ₃ H ₆ + <i>s</i> C ₄ H ₉	4.6 \times 10 ⁵	2.54	6756
3	JP7 + H \rightarrow CH ₃ + 1-C ₄ H ₈ + C ₃ H ₆ + <i>s</i> C ₄ H ₉	4.6 \times 10 ⁵	2.54	6756
4	JP7 + OH \rightarrow CH ₃ + 2C ₂ H ₄ + C ₃ H ₆ + C ₄ H ₇ + H ₂ O	3.0 \times 10 ⁴	2	−4000
5	JP7 + O ₂ \rightarrow CH ₃ + 2C ₂ H ₄ + C ₃ H ₆ + C ₄ H ₇ + HO ₂	8.0 \times 10 ¹¹		28000
6	JP7 + HO ₂ \rightarrow CH ₃ + 2C ₂ H ₄ + C ₃ H ₆ + C ₄ H ₇ + H ₂ O ₂	1.0 \times 10 ⁴	2.6	14000
7	JP7 + CH ₃ \rightarrow CH ₃ + 2C ₂ H ₄ + C ₃ H ₆ + C ₄ H ₇ + CH ₄	4.0 \times 10 ⁰	3.46	5480

^a The units of the rate parameters are cm, s, and cal. The empirical JP7 model was fitted to (a) the species concentration profiles after thermal cracking of JP7 in a turbulent flow reactor; (b) the laminar flame speeds of JP7, and (c) the ignition delay times of JP7-oxygen-argon mixture behind reflected shock waves. The model should be used with USC Mech II to provide detailed oxidation and pyrolytic kinetics for the cracking products.

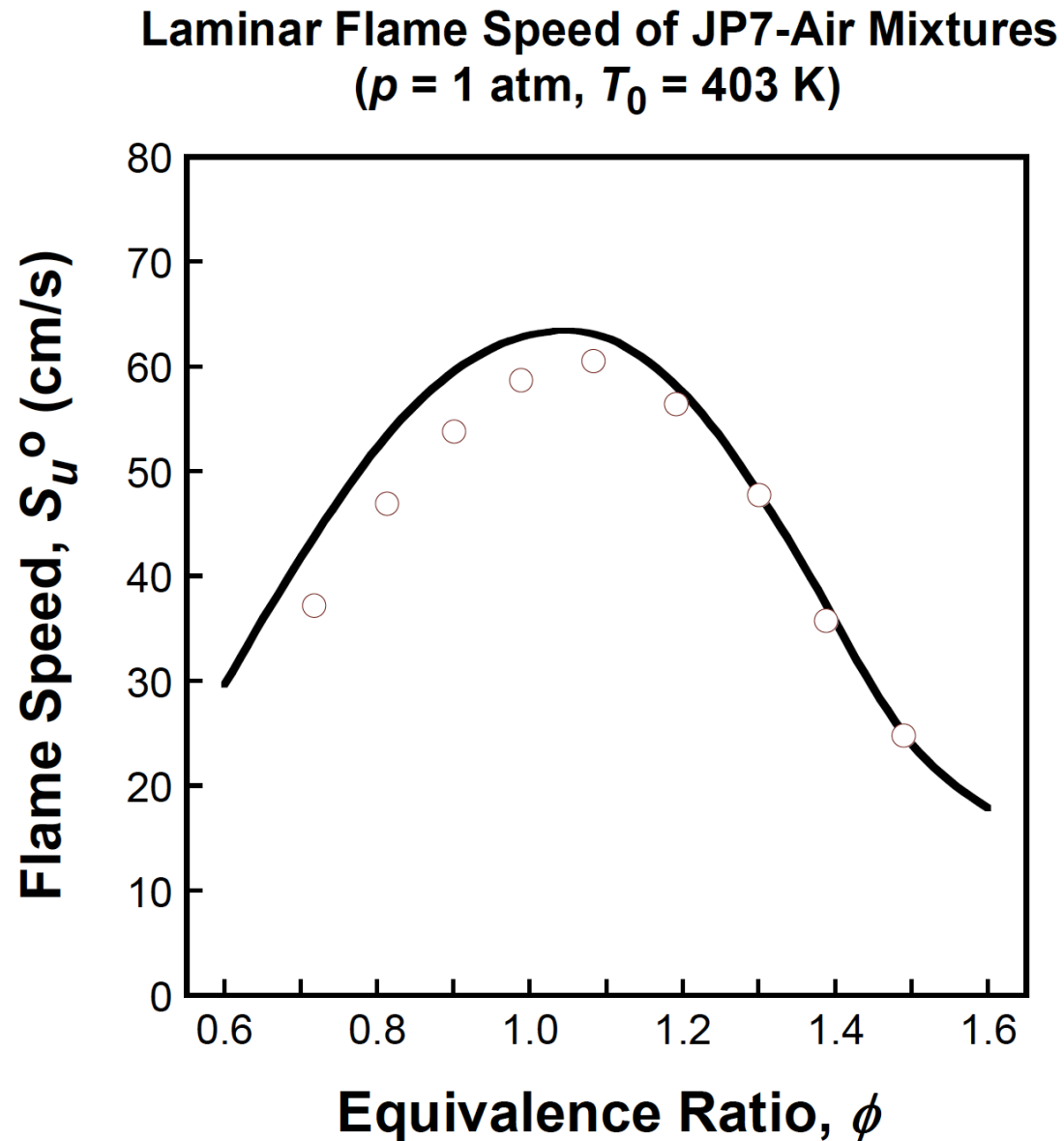
(2) Test the Idea Against JP7 – Selected Results



Data: Davidson, Haylett & Hanson, Combust. Flame (2008).

Wang & Egolfopoulos, unpublished

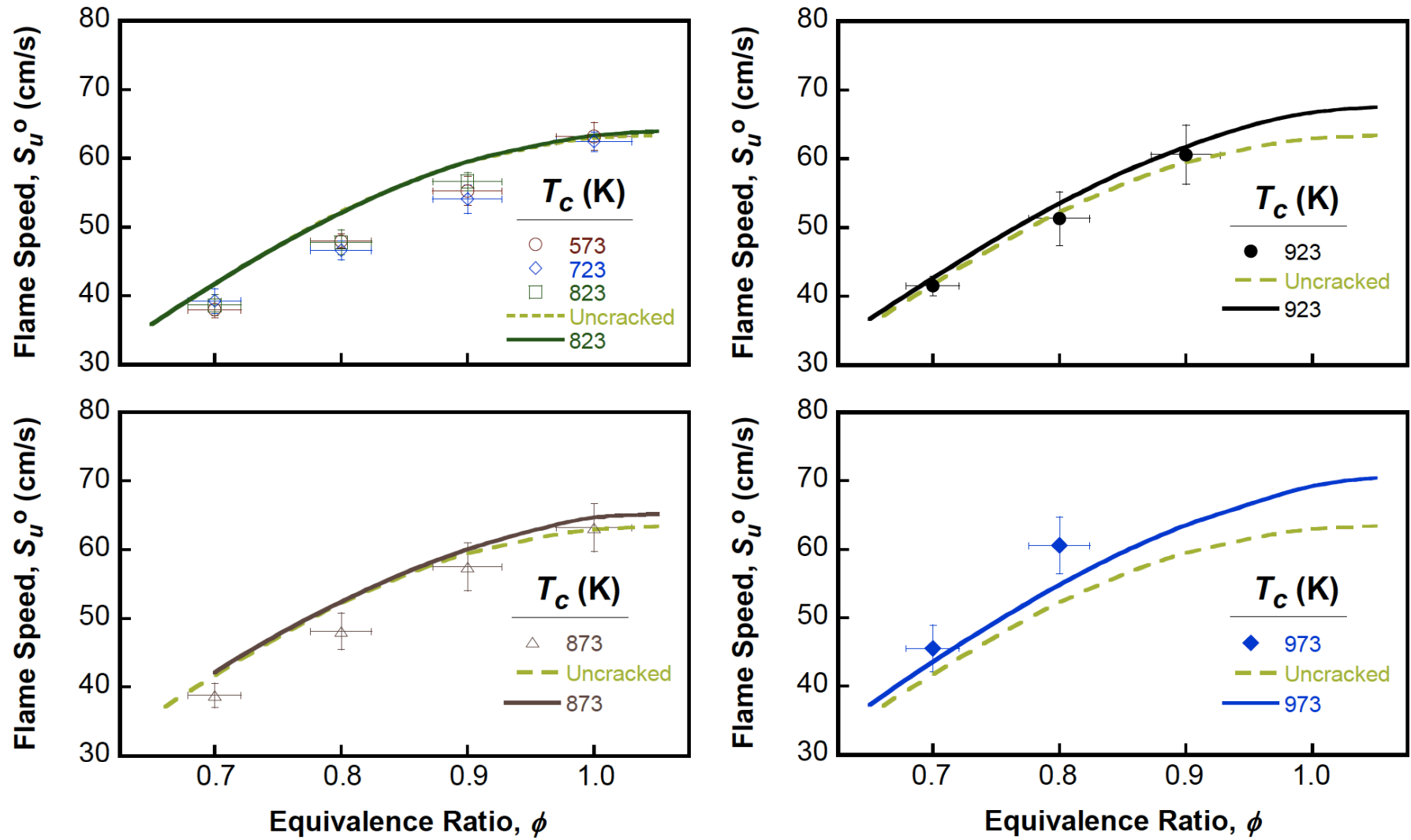
(2) Test the Idea Against JP7 – Selected Results



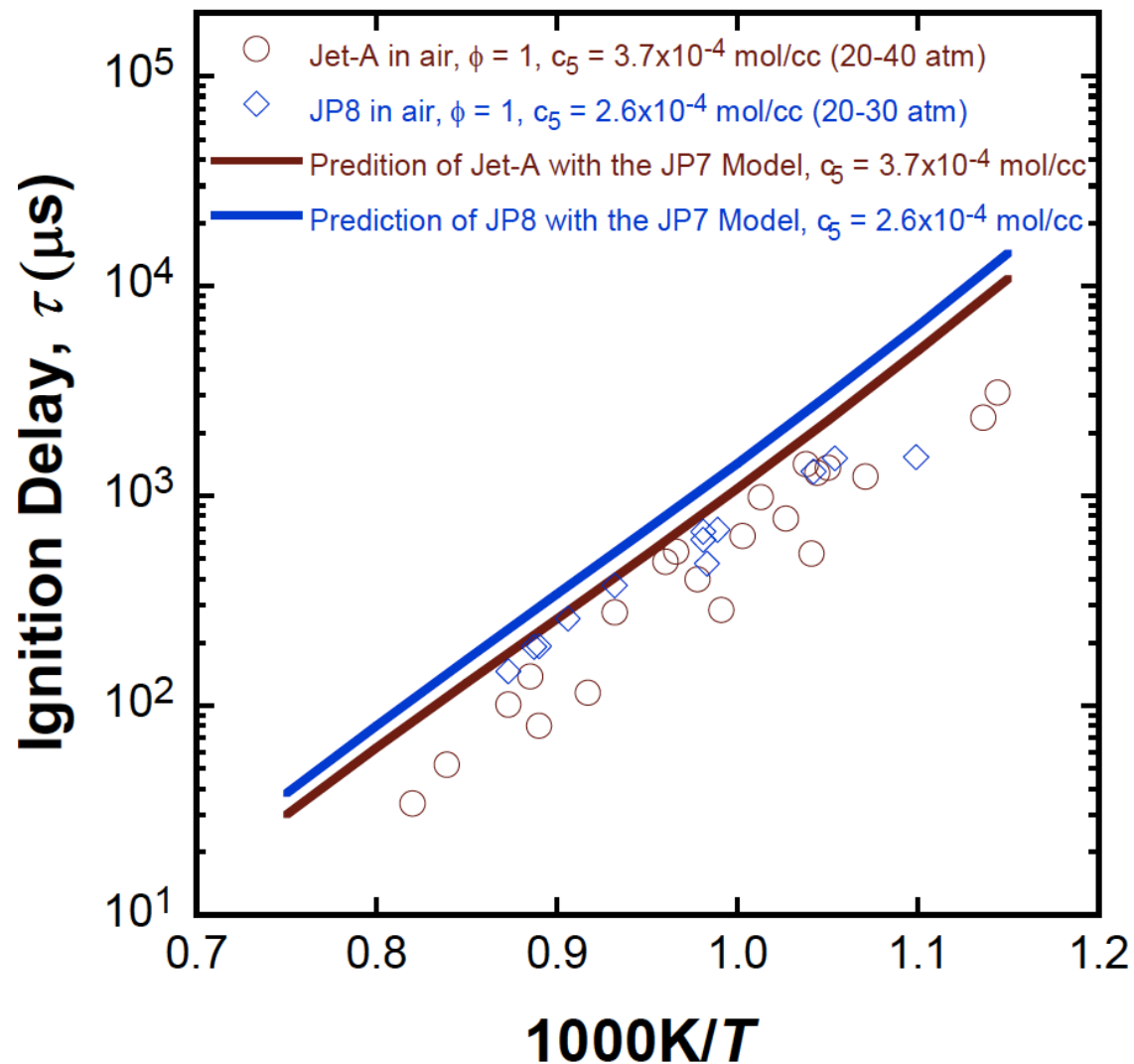
Wang & Egolfopoulos, unpublished

(2) Test the Idea Against JP7 – Selected Results

Flame speeds of cracked JP7 (1 atm, $T_0 = 403$ K): coupled JP7 cracking in a TFR and partially decomposed products burned in a Bunsen flame.



(2) Test the Idea Against JP8 and Jet-A – Selected Results



Data: Vasu, Davidson & Hanson, Combust. Flame (2008).

Wang & Egolfopoulos, unpublished

Conclusion

- An alternative surrogate method and approach is defined and demonstrated for a rather narrow range of conditions.
- The fundamental validity of the alternative approach is examined and justified.
- For flame phenomena fuel cracking is not rate limiting and may be decoupled from the oxidation kinetics of the cracked products.
- The composition of cracking products is critical to flame phenomena; the mathematical description of the low-D manifold(s) will be defined through experimentation.